AD-A084 169 VIRGINIA POLYTECHNIC INST AND STATE UNIV BLACKSBURG F/G 7/4
1H AND 13C FOURIER TRANSFORM NMR CHARACTERIZATION OF JET FUELS --ETC(U)
AUG 79 H C DORN N00173-78-C-0424

UNCLASSIFIED NL

1 OF 1
AD
A084169

END
DATE
FILMED
6-80
DTIC

LEVEL II

^{1}H AND ^{13}C FOURIER TRANSFORM NMR CHARACTERIZATION OF JET FUELS DERIVED FROM ALTERNATED ENERGY SOURCES

ADA084169

FINAL PROGRESS REPORT 23 Mar 78 - 30 Aug 79
FOR THE PERIOD

Mar. 23, 1978 - Aug. 30, 1979

H. C. DORN

VIRGINIA POLYTECHNIC INSTITUTE & STATE UNIVERSITY

PREPARED FOR
NAVAL RESEARCH LABORATORY
4555 OVERLOOK AVE.
WASHINGTON, D.C.
UNDER CONTRACT No. N00173-78-C-0424

Table of Contents

Final Progress Report
Naval Research Laboratory

Work Statement (See p. 7 of Contract)

1) ~~A Separation Study of Jet Fuel Samples Utilizing High Performance~~ Gel Permeation Liquid Chromatography

Initially, four jet samples were examined in this phase of the study using gel permeation liquid chromatography. We have previously discussed these results in the six month Progress Report. ~~(Appendix 1, p. 1)~~ Although the gel permeation approach has the advantage of nearly quantitative recovery from the chromatography column (typically greater than 95%) and high preparative loading, it suffers from two drawbacks in studies of the present jet fuels.

a) In general, the molecular weight and/or "size" of the compounds present in typical jet fuels do not cover a broad range. This is an obvious result of the relatively narrow distillation range(s) used to generate the jet fuels. That is, the gel permeation approach is more ideally suited in separations involving mixtures with a broad range in size and/or molecular weight (e.g., 100-1000 MW), whereas, the jet fuels have a more narrow range (e.g., 100-250 MW).

b) The available literature[1] indicates a paucity of model studies in gel permeation chromatography for understanding and/or predicting relative retention volumes which are appropriate for

jet fuel sample comparisons.

Based in part on the considerations above, we deemed it appropriate to first extensively examine the chromatographic behavior of jet fuels utilizing more commonly employed column packing materials silica gel and alumina which provide separations based on molecular polarity and/or functionality. We are not suggesting that gel permeation chromatography will not be important in separation studies of jet fuels, but rather, the silica gel and/or alumina represents a better reference point.

In addition, our ultimate aims for this portion of the research project have dramatically been revised during the last several months. That is, under a separate grant from DOE we have directly coupled a liquid chromatographic unit to ^{1}H FTNMR (LC-^{1}H NMR). With ^{1}H FTNMR serving as the on line detector for the chromatographic column. We have already completed a preliminary study of four jet fuels using this approach which was originally suggested as "Additional Exploratory Studies" 5b, p.8 of the present proposal. A manuscript[2] describing this recent work is presented in Appendix 2. We are elated with the initial results achieved and the ramifications of this approach to the study of jet fuels.

A number of important implications regarding the LC-^{1}H NMR approach are summarized below.

a) The use of freon 113(111- trichlorotrifluoroethane) (b.p.46°) as the chromatographic solvent appears to ideally mimic typical hydrocarbon solvents (e.g., hexane). Obviously, this solvent is ideal for the ^{1}H NMR detector since it contains no hydrogen.

b) The LC-^{1}H NMR profile for a given jet fuel requires only 30-40 minutes of experimental time and yet provides 40-50 ^{1}H NMR spectra representing 40-50 fractions. The time savings when compared with the laborious procedure normally employed consisting of LC fraction collection, removal of chromatographic solvent, preparation of sample for NMR examination, and finally examination of each separate fraction by ^{1}H NMR is at least a factor of 10 to 100.

c) The LC-^{1}H NMR profiles (See Appendix 2) for the jet fuels examined to date are unique "fingerprints" for each particular jet fuel. In addition, the LC-^{1}H NMR profiles clearly indicate further separations not apparent utilizing normal chromatographic detectors (e.g., Refractive Index detectors). For example, the LC-^{1}H NMR profiles clearly distinguish n-alkanes according to chain length as well as branched alkanes. Whereas, the corresponding Refractive Index traces reveal only the presence of one peak for all branched and n-alkanes.

d) The initial results obtained by the LC-^{1}H NMR suggest that LC-^{13}C NMR could be feasible with certain modifications. This is presently being pursued. However, the wealth of spectral information provided by the LC-^{1}H NMR could be sufficient for most samples.

In conclusion, we strongly hope that chromatographic efforts during the second year of this study will focus on the LC-^{1}H NMR and LC-^{13}C NMR approaches.

2) A Quantitative ^{1}H and ^{13}C FT NMR Study of "Synthetic Mixtures"

In this phase of the study the quantitative ^{1}H and ^{13}C FT NMR approach[3] was checked for accuracy with synthetic mixtures of known composition. The eight synthetic mixtures studied to date consist of twelve model compounds in each mixture. The actual sample composition data was previously reported (see Table I, Appendix 1). Also, aromatics (volume %) and freezing point data for these synthetic mixtures were previously reported (see Appendix 1, Figures 3 and 4) via ASTM procedures (ASTM D 1319-77) and (ASTM D 2386-67), respectively. The smoke point determinations (ASTM D 1322-75) for the synthetic mixture will be also discussed in conjunction with the jet fuels in the next section. In Table 1 the aromaticities (fa)[4] obtained by the ^{13}C FT NMR and aromatics, (volume %, ASTM D 1319-77) procedures are compared with actual known sample composition. In nearly every case the fa values obtained via the chromatographic ASTM procedure are higher than the actual values as expected since the ASTM procedure measures alkyl aromatics (e.g., ethylbenzene tetralin, etc.) as aromatics. It should also be noted that the ASTM procedure

measures volume % aromaticity, whereas, the ^{13}C FT NMR approach measures molar aromaticity.

The values reported in Table 1 for the ^{13}C FT NMR measurements represent the average of two different determinations. We estimate an error of $\pm$ 5% in the fa values reported (e.g., Sample #4, fa=20.4% $\pm$ 1%). The samples with very low fa values (e.g., Sample #1) would be expected to have a larger error because of the poorer $(\frac{S}{N})$obtainable in the aromatic region of ^{13}C spectrum. We believe that sample #4 could have a sample preparation error since the hydrogen aromaticity for this sample deviates in the same manner (see Table 2). The hydrogen aromaticity data is presented in Table 2 and indicates even better agreement with only Sample #4 deviating sharply (supra vida).

For the synthetic mixtures a reasonable correlation exists between the smoke point data and the aromaticities (fa) as indicated in Figure 1. However, it should be noted that the composition of these synthetic mixtures (Table 1, Appendix 1) is varied in a manner such that all important molecular parameters for the aromatic compounds are varied uniformily. That is, as one progresses from Sample #1 to Sample #8 the concentration of <u>all</u> of the aromatic compounds increase, instead of increasing a particular individual component. The latter method would provide a more reliable method for ascertaining the influences of a particular molecular parameter (e.g., aromatic substituted vs. unsubstituted carbons) on smoke points.

In conclusion, it is apparent from the limited model (6-8 synthetic mixtures) study that quantitative ^{1}H and ^{13}C FT NMR measurements are consistent with the calculated values (Tables 1 and 2). In the second year a more extensive set of synthetic mixtures should be studied. We plan to focus attention on the problem of varying a single molecular parameter (e.g., substituted aromatic carbons) and correlating this response with smoke point data. This approach could also be used with other physical properties (e.g., freezing points).

3) A Quantitative ^{1}H and ^{13}C FT NMR Study of Jet Fuels derived from Petroleum, Shale, Coal and Tar Sands

The original proposal called for examination of five to ten samples under this phase of the project. To date, we have actually examined 24 samples. Table 3 lists sample description data for the jet fuels. Basically, the first year was devoted to obtaining quantitative ^{1}H and ^{13}C FT NMR, elemental combustion: smoke point (ASTM D 1322-75) freezing point (ASTM D 2386-67) and aromatics (volume %) (ASTM D 1319-77) data for both petroleum and alternate energy jet fuels. We have previously reported some of this data (Appendix 1). In Table 4, ^{13}C FT NMR aromaticity (fa) and aromatics (volume %) data are compared. In virtually all cases the (fa) values obtained by the ASTM procedure are higher than the corresponding NMR values. The NMR derived values are higher than the ASTM values in only two cases (sample #11 and 18). We plan to recheck these two samples during the second year of this study. These results are consistent with the data obtained for the model studies (I,2), however, in the case of the jet fuels the deviations are much larger. The ^{13}C FT NMR data is based on two independent determinations in all

cases and we estimate a ± 5% error (e.g., sample #4, 27.2 ± 1.4%).

In Table 5 elemental combustion, ^{1}H and ^{13}C FT NMR data is tabulated for all the jet fuels. Average molecular parameters (e.g., (H/C)ar, (H/C)al, etc.) are tabulated for each jet fuel.[7] In certain cases (e.g., Sample #14) the data is obviously in error for the (H/C)ar value. It should be remembered that this parameter is derived from all three measurements, that is, elemental combustion, ^{1}H and ^{13}C FT NMR. In view of this, relatively large errors would be expected for this parameter. In addition, when the fa^{C} values are relatively low, a poorer $(\frac{S}{N})$ in the aromatic region of ^{13}C spectrum also leads to larger errors in this derived parameter. During the second year, we plan to recheck several samples reported in Table 5.

In Table 6, the smoke point, freezing point, and aromaticity data is tabulated for all of the jet fuels. This data was obtained by ASTM procedures (D 1322-75, D 2386-67 and D 1319-77), respectively.

With the data base presented in Tables 4-6 correlations were attempted between the NMR derived molecular parameters and various physical properties. Specifically, a rough correlation does exist between smoke points for jet fuels and aromatics (volume %) via ASTM procedure). The correlation does not change significantly using ^{13}C NMR derived aromaticities (See Figure 2). The synthetic mixture data is also plotted in Figure 1 for comparative purposes. Superficially, it appears that jet fuels with approximately the same aromaticities as certain synthetic mixtures (e.g., sample #11,

#16 and #18 compared with synthetic mixture, 9.5%) have higher smoke points for the same aromaticity.

In order to further disect the importance of various aromaticity parameters, we hypothetically state that three distinct types of aromatic carbons should influence smoke points. The three types are illustrated for m-xylene and naphthalene below.



That is, Cu, Cs and Cs' represent unsubstituted, substituted (alkyl) and substituted (ring junction) aromatic carbons, respectively. Using this nomenclature aromaticity fa^C and fa^H can be recast in the forms shown below.

$$fa^C = \frac{Cu+Cs+Cs'}{C_T} \qquad 1)$$

$$fa^H = \frac{Har}{H_T} = \frac{Cu}{H_T} \qquad 2)$$

Multiplying 2) by $(H/C)_T$ via elemental combustion data yields 3) below:

$$(H/C)_T\left(\frac{Cu}{H_T}\right) = \frac{Cu}{C_T} \qquad 3)$$

Subtracting equations 1) from 3) yields:

$$\frac{Cu+Cs+Cs'}{C_T} - \frac{Cu}{C_T} = \frac{Cs+Cs'}{C_T} \qquad 4)$$

Equation 4) represents the fraction of total carbon which is substituted aromatic carbon. A further separation of Cs from Cs' is not readily possible from the available data.[6] Figure 3 is a plot of $\left(\frac{Car - Har}{C_T} = \frac{Cs + Cs'}{C_T}\right)$ versus the smoke point for the jet fuels. An interesting feature is now apparent in this plot. Namely, all jet fuels with carbon aromaticities (fa^C) above 9% now correlate reasonably well with the synthetic mixtures. In fact, the jet fuels which do not correlate well are the same ones which yielded unreasonable (H/C)ar in Table 5 (e.g., sample #14 and #9). It should be emphasized again that jet fuels with ^{13}C FT NMR aromaticities less than 6-9% have a larger error because of lower inherent $(\frac{S}{N})$ ratios for the ^{13}C aromatic regions. In addition, it should be noted that aromaticities less than 6-9% approach comparable levels of alkene content (2-4%, via ASTM procedures). If one excludes all samples in Figure 3 with aromaticities less than 9% a remarkably good correlation for both the synthetic mixtures and the remaining jet fuels results as indicated in Figure 4. The remaining points that sharply deviate (sample #16 and #17) have fa^C values close to 10%. We conclude that substituted aromatic carbon content (Cs + Cs') plays a dominant role in correlating smoke points.

We have also found that the linear alkane length of jet fuels correlate reasonably well with fuel freezing points (see Figure 5). The average linear n-alkane length is obtained directly from ^{13}C FT NMR spectral parameters.[7] It is remarkable that a correlation even exists since contributions from other components in the mixture and their respective concentrations are known to contribute to jet fuel freezing points.[8]

During the second year, we plan to examine this problem in more depth utilizing the synthetic mixture approach. That is, varying the concentration of a single molecular parameter within a synthetic mixture should provide empirical data regarding the influence of these parameters on freezing points. This is analogous to the approach previously suggested for aromaticity parameters.

In this report we have not presented copies of the ^{13}C and ^{1}H FT NMR spectra. These are stored on magnetic tape files and can be provided upon request.

4) Exploration of Double Resonance NMR Techniques for Fuel Analysis

This study was suggested in the original proposal (Phase III, p. 10) as an exploratory study if time permitted during the first year. Unfortunately, we can not report any results in this portion of the study to date. However, the acquisition of new NMR equipment will more readily facilitate these studies during the second year.

5) Development of a Computer Program to Predict and Quantify Components Present in Jet Fuels Utilizing ^{1}H and ^{13}C FT NMR Data as Input Parameters

This study was also suggested in the original proposal (Phase III, p. 10) as an exploratory study if time permitted during the first year. We have started to modify a mass-spectrometer program for this purpose. Unfortunately, the individual working on this portion of the project decided to leave the project. This has virtually stopped all work on this portion of the proposal. The development of these computer programs will become crucial in the 2nd and 3rd year as our data base (I, 1 and 2) increases. We hope to focus more attention on this portion of the proposal during the second year.

II. TABLES

Table 1

Synthetic Models -
Comparison of Aromaticity Values (fa) derived
from ^{13}CFTNMR, Aromatics (volume %) and Calculated Values

Synthetic Mixture #	fa(^{13}CNMR)[1]	Aromatics (Volume %)[2]	fa(calculated)[3]
1	2.4	3.5	2.0
2	10.1	10.4	9.5
3	17.5	-	16.5
4	20.1	17.0	17.5
5	27.0	26.5	25.5
6	29.4	32.8	30.0
7	-	52	44.5
8	71.8	96	76.0*

[1]Molar fa values obtained from ^{13}CFTNMR spectra $\left(\frac{C_{ar}}{C_{total}}\right)$x100

[2]Volume % aromatic content obtained from ASTM Procedure, (D 1319-77)

[3] Calculated values see Table 1, Appendix 1

*Sample 8 reported as 80% in Table 1 of Appendix 1, actual fa value is 76% because of an error in sample preparation.

Table 2

Synthetic Models -
Comparison of Hydrogen Aromaticity Values and Calculated Values

Synthetic Mixture #	H_{ar}/H_{total} (%) (^1H NMR)[1]	H_{ar}/H_{total} (%) (calculated)[2]
1	1.0	1.0
2	3.1	3.3
3	6.6	6.2
4	7.6	6.7
5	10	10
6	12	12
7	22	25
8*	55	55

[1]Molar fa values obtained from ^1H FTNMR $\left(\frac{H_{ar}}{H_{total}}\right)x100$

[2]Calculated values see Table 1, Appendix 1

*Sample 8 reported as 80% in Table 1 of Appendix 1, actual fa value is 76% because of error in sample preparation.

Table 3

Jet Fuel Samples and Source*

Sample #	
1	Sample VI/NR-77-01, Modified JP-4 This sample was blended especially for a combustion test program, which had as its purpose the definition of fuel chemistry effects on engine performance. The basic JP-4 fuel was blended with a highly aromatic solvent (containing mainly xylenes) to give an aromatic content above 35%.
2	Sample VI/NR-77-02, Modified JP-8 U.S. Air Force via Dr. Butler
3	Sample VI/NR-77-03, JP-8 This sample is a baseline, unmodified JP-8 fuel used in a combustion test program conducted by one of the major engine manufacturers.
4	Sample VI/NR-77-04, Modified JP-8 This sample was blended for a combustion test program, to determine the effect of increased aromatics content on engine performance. The baseline JP-8 was blended with a highly atomatic solvent (primarily xylenes) to give an aromatic content above 35%.
5	Sample VI/NR-77-05, Modified JP-8 This sample was blended for a combustion test program by one of the major jet engine manufacturers. Purpose is to determine the effect of extending the boiling range of the fuel upon engine performance. The boiling range was extended by blending with about 12% of a paraffinic light mineral oil.
6	Sample VI/NR-77-06, Routine JP-7 Received from USAF quality control laboratory; represents a routine JP-7 procurement from a major refiner.
7	Sample VI/NR-77-07, Routine JP-7 Received from USAF quality control laboratory; represents a 383,000 gallon batch of JP-7 purchased from a major refiner.
8	Sample VI/NR-77-08, Experimental Fuel This is an experimental turbine engine fuel of uncertain history.

Table 3 Continued

Sample #	
9	<u>Sample VI/NR-77-09, Routine Jet-A</u> Received from USAF quality control laboratory; represents a 45,000 gallon batch of Jet-A from a commercial refinery. (U.S. Air Force via A. Butler).
10	<u>Sample VI/NR-77-10, Specification JP-7</u> (U.S. Air Force via Dr. Butler)
11	<u>Sample VI/NR-77-11, Shale Oil JP-4</u> (U.S. Air Force via Dr. Butler)
12	<u>Sample VI/NR-77-12, Shale Oil Jet A</u> (U.S. Air Force via Dr. Butler)
13	<u>Sample VI/NR-77-13, Routine JP-4</u> Received from USAF quality control laboratory; represents a 45,000 barrel batch of routine JP-4 purchased from a major refinery.
14	<u>Sample VI/NR-77-14, Routine JP-4</u> Received from USAF quality control laboratory; represents a 49,500 gallon batch of routine JP-4 purchased from a commercial source.
15	<u>Sample VI/NR-77-15, Routine JP-4</u> Received from USAF quality control laboratory; represents a 420,000 gallon batch of routine JP-4 purchased from a major refinery.
16	<u>Sample VI/NR-77-16, Routine JP-4</u> Received from USAF quality control laboratory; represents a 950,000 gallon batch of routine JP-4 purchased from a commercial supplier.
17	<u>Sample VI/NR-77-17, Specification JP-4</u> (U.S. Air Force via Dr. Butler)
18	<u>Sample VI/NR-77-18, Specification JP-4</u> (U.S. Air Force via Dr. Butler)

Table 3 Continued

Sample #	
19	Sample VI/NR-77-19, Specification JP-8 (U.S. Air Force via Dr. Butler)
20	Shale Paraho, JP-5 (NRL via Dr. Hazlett)
21	Coal coed process, JP-5 (NRL via Dr. Hazlett)
22	NASA #4 Jet A, Shale (TOSCO) (NRL via Dr. Hazlett)
23	NASA #5 Jet A, (H-Coal) (NRL via Dr. Hazlett)
24	NASA #6 Jet A, (H-Coal) (NRL via Dr. Hazlett)

*) Samples 1-19 obtained from Dr. R. Butler, U.S.A.F.

Table 4

Fuel Aromaticity (fa) and Aromatics

Sample #	fa(NMR) %[1]	Aromatics (Volume %)[2]
-01	37.2	38.9
-02	4.5	20
-03	8.8	15.2
-04	27.2	34.8
-05	7.8	16.0
-06	3.2	6
-07	4.5	4.6
-08	6.0	6.3
-09	6.5	22
-10	3.5	4.7
-11	11.1	7
-12	13.7	23
-13	7.6	10
-14	6.1	10
-15	6.9	8.2
-16	11.8	13
-17	12.2	13
-18	10.1	8.4
-19	9.7	10
-20	17.2	26.0
-21	15.8	25.0
-22	8.8	14
-23	18.8	39
-24	5.1	8

[1] Molar fa values obtained from ^{13}CFTNMR spectra $(\frac{C_{ar}}{C_{total}})$x100

[2] Volume % aromatic values obtained from ASTM Procedure (D 1319-77)

Table 5

^{1}H and ^{13}C NMR Derived Molecular Parameters

Sample#	% H_{total}	% C_{total}	(H/C)T	fa^C	fa^H	(H/C)ar	(H/C)al	Linear Alkane Ave. Length
1	12.01	88.37	1.63	37.2	15.3	.67	2.20	8.6
2	14.38	85.73	2.01	4.5	1.5	.66	2.08	9.6
3	14.10	86.25	1.96	8.8	3.6	.80	2.07	10.4
4	12.32	87.75	1.68	27.2	9.7	.60	2.09	10.0
5	13.91	86.35	1.93	7.8	3.8	.94	2.02	11.0
6	14.98	85.24	2.11	3.2	1.0	.63	2.16	9.6
7	14.91	85.09	2.10	4.5	0.9	.43	2.18	9.2
8	14.80	85.19	2.08	6.0	1.0	.32	2.20	10.1
9	13.86	86.16	1.93	6.5	3.3	.99	2.00	10.3
10	14.80	85.19	2.08	3.5	0.7	.41	2.15	10.4
11	14.17	85.91	1.98	11.1	4.0	.71	2.14	-
12	13.84	86.44	1.92	13.7	3.6	.51	2.15	9.9
13	14.49	85.57	2.03	7.6	3.0	.81	2.13	8.0
14	14.79	85.33	2.08	6.1	3.4	1.16	2.14	9.8
15	14.31	86.01	2.00	6.9	2.5	.72	2.09	8.1

Table 5 (Cont'd)

^{1}H and ^{13}C NMR Derived Molecular Paramters (Cont'd)

Sample#	(% H_{total})[1]	(% C_{total})[1]	$(H/C)_T$[2]	(fa^C)[3]	(fa^H)[4]	$(H/C)ar$[5]	$(H/C)al$[6]	Linear Alkane Ave. Length[7]
16	14.08	85.92	1.97	11.8	4.3	.71	2.13	8.5
17	14.30	86.05	1.99	12.2	4.6	.75	2.17	7.6
18	14.77	84.99	2.09	10.1	2.2	.45	2.27	8.6
19	14.20	85.82	1.99	9.7	3.2	.65	2.13	7.9
20	14.01	86.10	1.99	17.2	3.4	.39	2.28	-
21	12.97	86.82	1.77	15.8	4.4	.50	2.04	-
22	14.23	85.96	1.92	8.8	2.9	.66	2.12	8.9
23	12.91	87.32	1.95	18.8	5.7	.53	2.06	-
24	13.79	86.14	1.79	5.1	1.4	.54	2.00	13.8

[1] Values are from elemental combustion analysis

[2] $(H/C)_T$ = the total hydrogen to carbon ratio

[3] fa^C = the aromatic carbon to total carbon ratio (aromaticity)

[4] fa^H = the aromatic hydrogen to total hydrogen ratio

[5] $(H/C)ar$ = the aromatic hydrogen to carbon ratio

[6] $(H/C)al$ = the aliphatic hydrogen to carbon ratio

[7] Values obtained from ^{13}C FT NMR spectra by integration of appropiate region for methyl (CH_3) and methylene ($-CH_2-$) regions for $CH_3-(CH_2)_n-CH_3$,

Table 6

Freezing Point, Aromatics, and Smoke
Point Data for the Jet Fuels (via ASTM Procedures)

Sample #	Freezing Point(°C)	Aromatics (Volume %)	Smoke Point
1	-48	45	12.0
2	-31	20	28.6
3	-43	17	29.6
4	-51	34.8	14.0
5	-30	22	26.5
6	-44.5	6	37.1
7	-44	4.6	44.8
8	-48	6.3	38.0
9	-50	22	25.8
10	-46	4.7	39.0
11	-56	7	38.0
12	-34	23	25.0
13	-60.5	10	36.0
14	-54	10	30.1
15	-66	4	34.2
16	-63.5	13	34.0
17	-72	13	25.2
18	-63	8.4	36.0
19	-72	10	22.6
20	-29	26	12.0
21	-72	25	19.1
22	-72	14	24.5
23	-72	39	15.1
24	-72	8	21.8

III. FIGURES

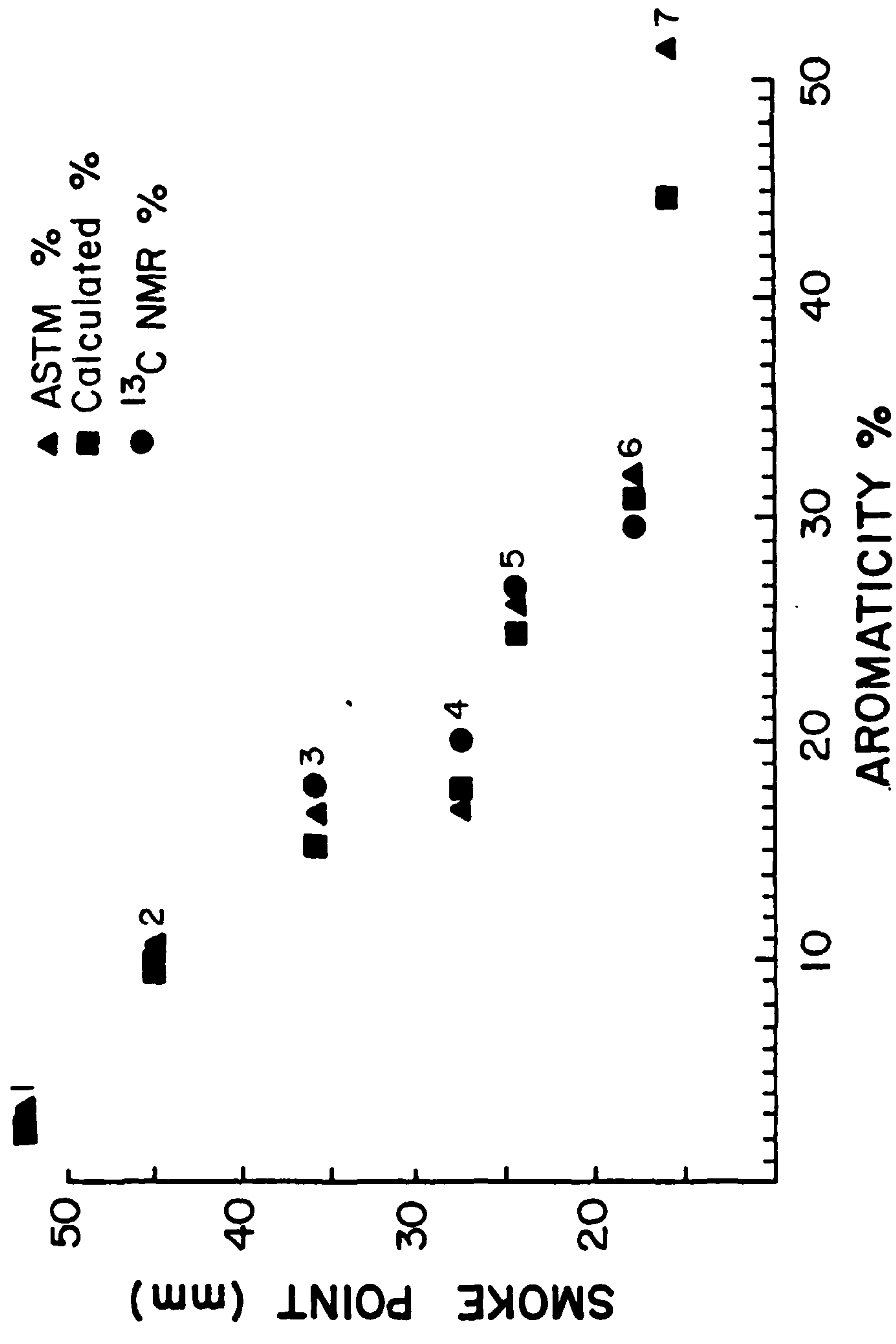

▲ ASTM %
■ Calculated %
● 13C NMR %
SMOKE POINT (mm)
AROMATICITY %
50
40
30
20
10
1
2
3
4
5
6
7

FIGURE 2

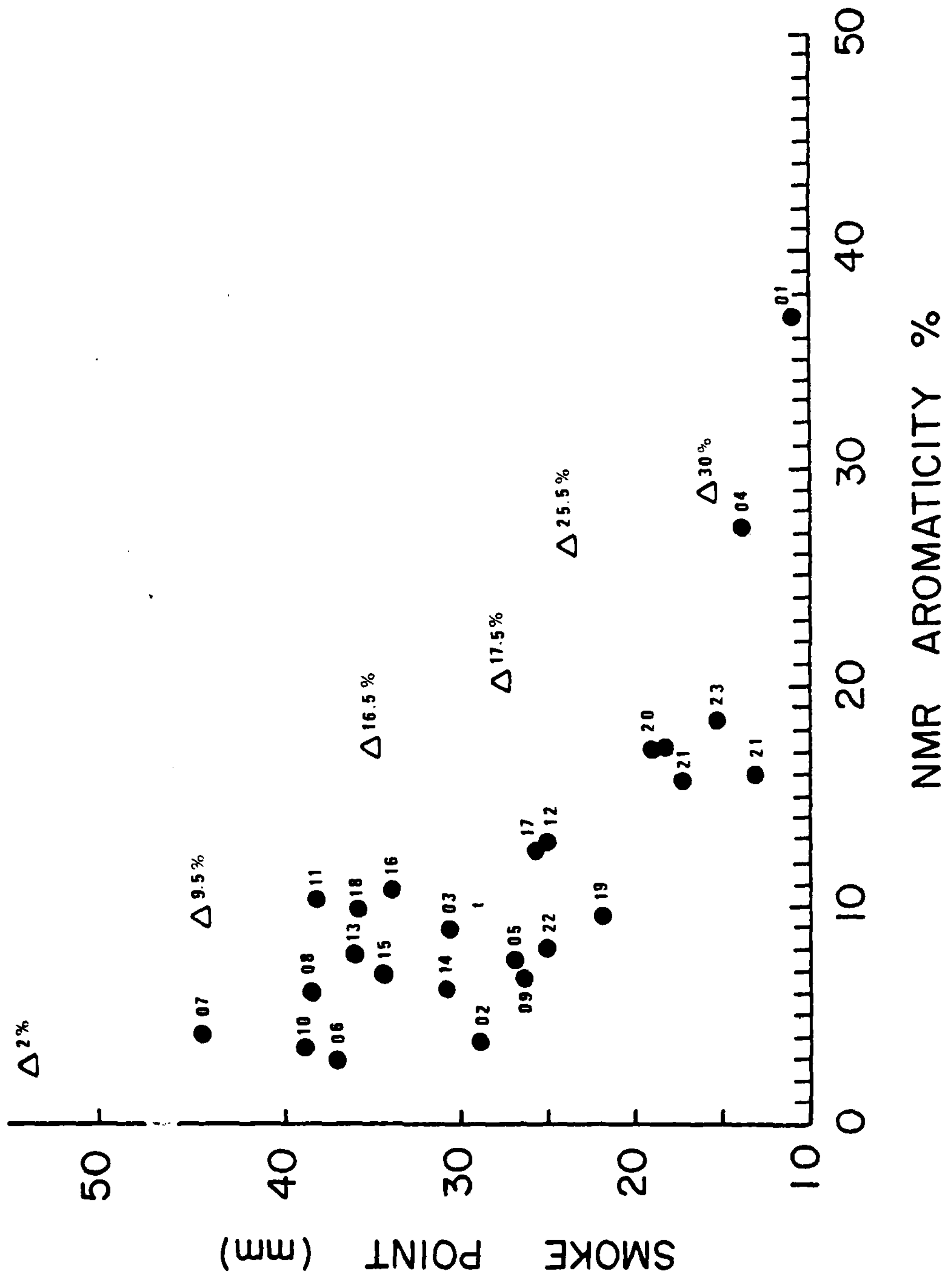

SMOKE POINT (mm)
NMR AROMATICITY %
10
20
30
40
50
0
Δ 2%
Δ 9.5%
Δ 16.5%
Δ 17.5%
Δ 25.5%
Δ 30%

FIGURE 3

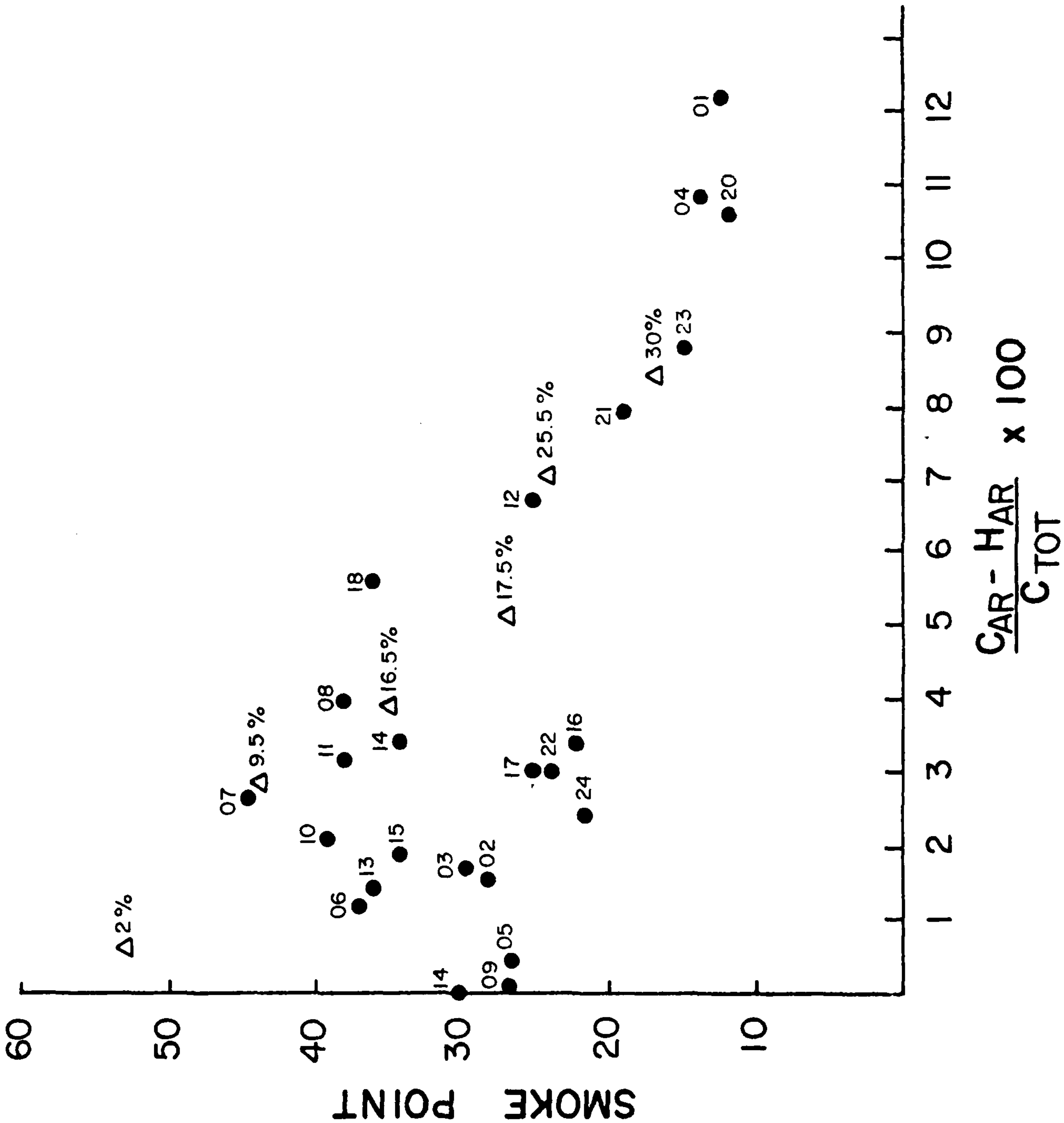

SMOKE POINT
$\frac{C_{AR} - H_{AR}}{C_{TOT}} \times 100$
Δ 2%
Δ 9.5%
Δ 16.5%
Δ 17.5%
Δ 25.5 %
Δ 30%

FIGURE 4

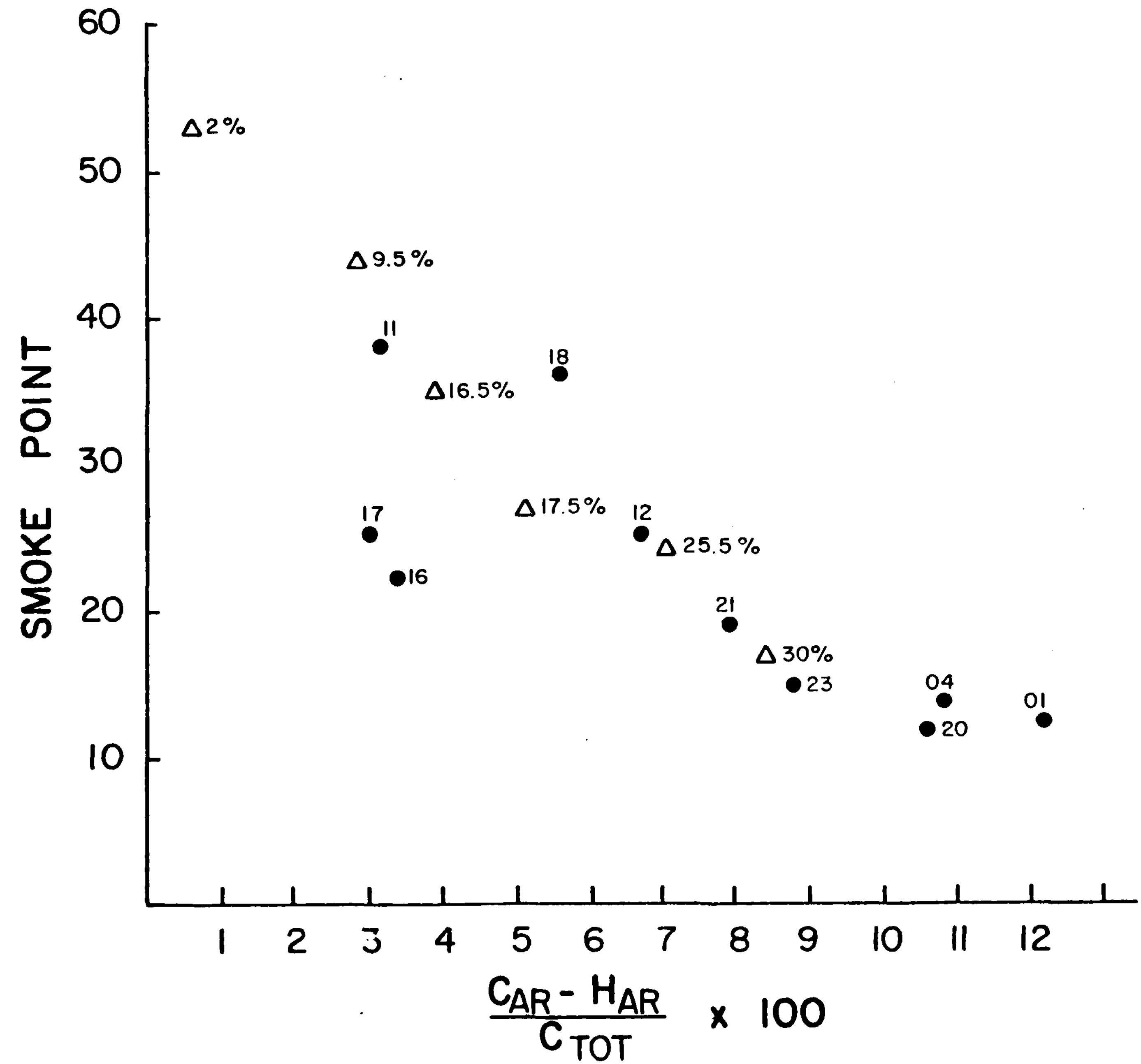
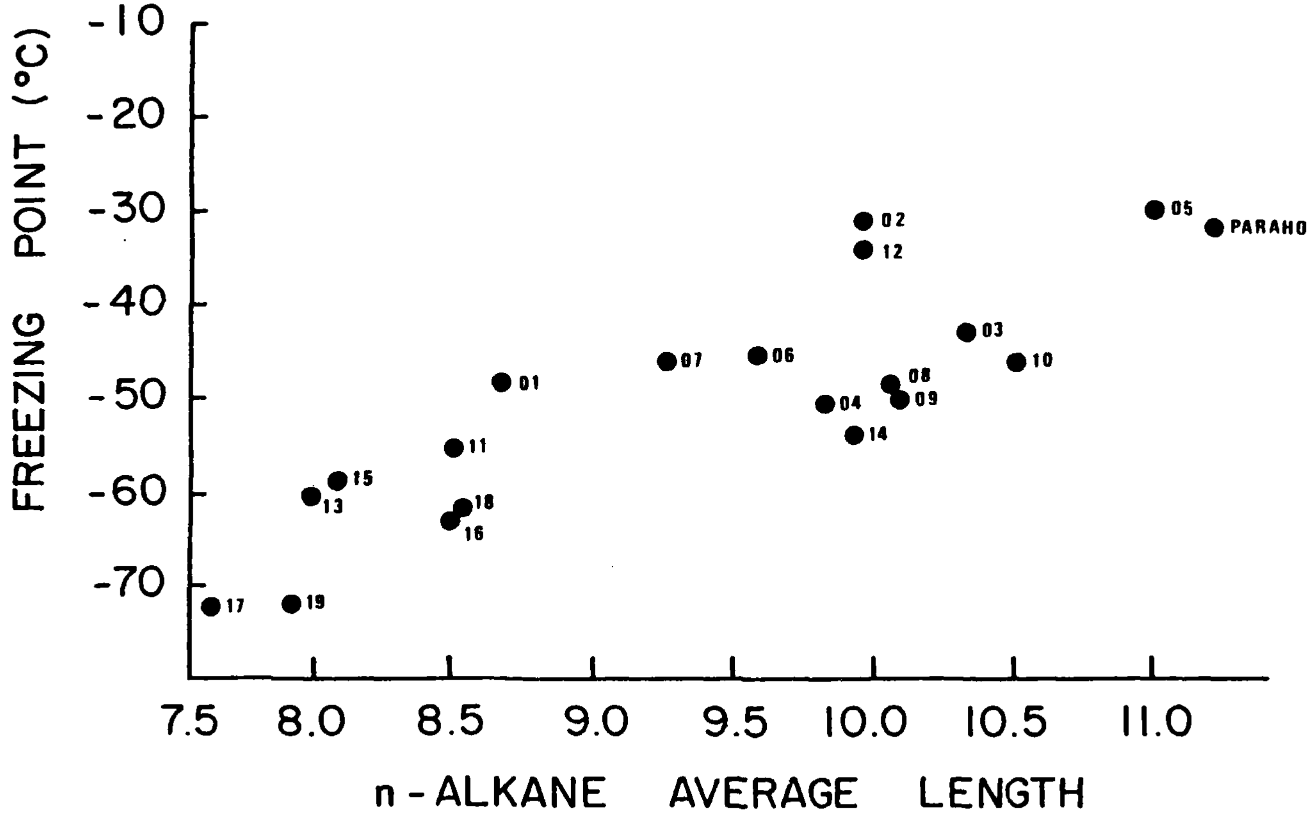

SMOKE POINT
60
50
40
30
20
10
1 2 3 4 5 6 7 8 9 10 11 12
$\frac{C_{AR} - H_{AR}}{C_{TOT}} \times 100$
Δ2%
Δ9.5%
Δ16.5%
Δ17.5%
Δ25.5%
Δ30%
11
18
17
16
12
21
23
04
20
01

FIGURE 5


FREEZING POINT (°C)
-10
-20
-30
-40
-50
-60
-70
n-ALKANE AVERAGE LENGTH
7.5
8.0
8.5
9.0
9.5
10.0
10.5
11.0
17
19
13
15
11
18
16
01
07
06
04
14
02
12
08
09
03
10
05
PARAHO

IV. Personnel Participating in Project

Principal Investigator: H. C. Dorn

Individual	Work Area
Tom Glass	^{1}H and ^{13}C FT NMR, LC-^{1}H NMR
Doug Hausler	Chromatography, LC-^{1}H NMR
Edwige Denyszyn (Technician)	ASTM procedures and sample preparation
Debbie Crowther*	Model Studies and Computer Programming
Jim Haw	Chromatography and LC-^{1}H NMR
Dr. Ed Motell**	LC-^{1}H NMR
Dr. Larry Taylor	Consultant for some of the chromatographic work

*) Decided to leave project, August, 1979

**) Visiting Professor, San Francisco State University

REFERENCES AND GLOSSARY

1) D. W. Hausler, J. W. Hellgeth, H. M. McNair, L. T. Taylor, J. Chromatog. Sci., 17 617 (1979).

2) Manuscript submitted to Anal. Chem., Nov., 1979.

3) The quantitative ^{13}C FT NMR approach is basically the same utilized for previous model and coal fraction studies, see for example; a) H. C. Dorn and D. L. Wooton, Anal. Chem., 48, 2146 (1976); b) D. L. Wooton, W. M. Coleman, L. T. Taylor and H. C. Dorn, Fuel, 57, 17 (1978); c) D. L. Wooton, W. M. Coleman, T. E. Glass, H. C. Dorn and L. T.Taylor, Advances in Chemistry Series, No. 170, 37 (1978) and; d) H. C. Dorn, L. T. Taylor and T. E. Glass, Anal. Chem., 51, 947 (1979). A Jeolco PS-100 nuclear magnetic resonance spectrometer was used to obtain the ^{1}H and ^{13}C spectra at 100.0 and 25.1 MHz, respectively. The spectrometer was used in both the continuous wave (CW) and the Fourier transform (FT) modes for the ^{1}H spectra; however, only the Fourier transform mode was used for the ^{13}C spectra. In addition, a Varian EM-390 was used to obtain some of the CW ^{1}H NMR data at 90 MHz. The FT spectra were obtained with a Digilab FTS-3-NMR data system. All ^{13}C NMR integrations utilized double precision software provided by the Digilab data system. The ^{1}H gated decoupling technique was employed for the ^{13}C NMR measurements for suppression of long T_1 and nuclear Overhauser effects. In this mode, the ^{1}H decoupler was on only during the time interval that the ^{13}C magnetization was being monitored (t) and off for a longer time (T). The intervals for t and T employed were 0.65 and 4.35 s, respectively, with 8192 points per spectrum.

Initial experiments varying the value of T for fraction 30 indicated that the ^{13}C integrals did not change for $T \geq 2s$. The data acquisition time (t) and the number of data points (8192) were the same in both the ^{1}H and the ^{13}C NMR measurements.

The samples were prepared by weighing the reference hexamethyldisiloxane and $Fe(acac)_3$ directly into the NMR tube containing chloroform-d as the solvent. The capped NMR samples were stored at -10°C in a cold storage room during the interval between the ^{1}H and ^{13}C NMR measurements. A typical jet fuel sample contained 1.2 g of fuel, 60 mg of chromium acetylacetonate $Cr(AcAc)_3$ 1 g of d_1-chloroform, and 300 mg of hexamethyldisiloxane (HMDS).

4) All ^{13}C NMR aromaticities were obtained by integrating the ^{13}C aromatic spectral region relative to the total integral, that is, $(fa^C = \frac{C_{ar}}{C_T})$. The hydrogen aromaticities were obtained in a similar manner from the ^1H spectra $(fa^H = \frac{H_{ar}}{H_T})$.

5) The $(H/C)_{ar}$ and $(H/C)_{al}$ ratio were obtained utilizing elemental combustion, ^1H and ^{13}C NMR data. For example,

$$(H/C)_{ar} = \left(\frac{H_{ar}}{H_T}\right)\left(\frac{C_T}{C_{ar}}\right)\left(\frac{H}{C}\right)_T$$

$\left(\frac{H_{ar}}{H_T}\right)$ ↑ ^1HNMR; $\left(\frac{C_T}{C_{ar}}\right)$ ↑ ^{13}CNMR; $\left(\frac{H}{C}\right)_T$ ← *elemental combustion*

6) The LC-^1H NMR would readily allow separation of this parameters (Cs from Cs') since alkylaromatics and naphthalenes have significantly different retention volumes.

7) Values obtained from ^{13}C FT NMR integration of appropriate spectral regions for methyl($-CH_3$) and methylene($-CH_2-$) groups for n-alkanes ($CH_3-(CH_2)_n-CH_3$). It should be noted that spectral overlap problems in the ^{13}C FT spectra in some cases hinder determination of this parameter. This problem would be totally avoided in the LC-^1H NMR approach since linear alkanes appear in completely separate fractions.

8) W. Affens, "Freezing Point Relationships of Jet Fuels", abstract of paper presented at Vaval Research Laboratory Workshop on Basic Research Needs for Synthetic Hydrocarbon Jet Aircraft Fuels, June 15 & 16, 1978, p. 187.

VI. APPENDICES

^1H AND ^{13}C FOURIER TRANSFORM NMR CHARACTERIZATION OF JET FUELS DERIVED FROM ALTERNATED ENERGY SOURCES

SIX MONTH PROGRESS REPORT FOR
THE PERIOD

MAR. 23, 1978 - AUG. 23, 1978

H. C. DORN

VIRGINIA POLYTECHNIC INSTITUTE & STATE
UNIVERSITY

PREPARED FOR
NAVAL RESEARCH LABORATORY
4555 OVERLOOK AVE.,
WASHINGTON, D.C.
UNDER CONTRACT No. N00173-78-0424

Six Month Progress Report

Naval Research Laboratory
Contract No. N00173-78-C-0424

Work Statement (see p. 7 of Contract)

1. A Separation Study of Jet Fuel Samples Utilizing High Performance Gel Permeation Liquid Chromatography

To date, we have examined four jet fuel samples in this phase of the study. Figures 1 and 2 are chromatograms for these samples with the column chromatographic conditions indicated in the figure captions. In comparing the JP-4 and modified JP-4 (modified by adding ~35% xylene mixture) chromatograms in Figure 1, it is apparent that the smaller peak for the JP-4 sample represents hydrocarbons which undoubtedly are C_8 or greater. This is also suggested by the JP-8 and modified JP-8 (modified by adding paraffins) chromatograms presented in Figure 2 where the peak maximizes at a lower retention volume (~20.5 ml).

These initial results indicate that at least a partial preparative separation (2-3 fractions) could be achieved. Based on these results and a related model study (submitted to Anal. Chem.), we believe hydrocarbons (aromatics and aliphatics) C_8-C_{10} or smaller could be effectively separated from higher molecular weight hydrocarbons. Since preparative chromagraphic fractions (~0.05-0.2 g of sample) are obtained in 20-30 minutes, ^1H and ^{13}C FT nmr examination of these fractions is now feasible. We plan to pursue examination of these fractions during the next four months.

2. A Quantitative ^1H and ^{13}C FT NMR Study of Synthetic Mixtures

We have purchased ~80 pure model hydrocarbons to prepare sets of synthetic mixtures. To date, we have prepared eight mixtures containing various amounts of twelve components. The components and weight % data for these "standard

mixtures" are presented in Table 1. For comparative purposes, we have obtained aromaticity and freezing point data for these synthetic mixtures via ASTM procedures (1319-77) and (2386-67), respectively. This data is presented graphically in Figures 3 and 4. We have purchased the apparatus necessary for smoke point determinations (~1 month delivery) which will be used to obtain smoke point data for the synthetic mixtures and the jet fuel samples.

Although we will not report any of the ^{1}H and ^{13}C FT nmr data for these synthetic mixtures in this report, the experimental phase of this work will be completed (8 synthetic mixtures) in the next two weeks.

3. A Quantitative ^{1}H and ^{13}C FT NMR Study of Jet Fuels from Petroleum, Shale, Coal and Tar Sands

For comparative purposes and in a similar manner to the synthetic mixture work (item 2) above, we have measured aromaticity and freezing point data via ASTM procedures (1319-77) and (2386-67), respectively, for the 24 jet fuel samples "in house". Description and source data are presented in Table 2. The aromaticity data for the JP-4, JP-7 and JP-8, and alternate energy fuels are presented graphically in Figures 5, 6, and 7, respectively. In the same manner, the freezing point data is presented in Figures 8, 9 and 10.

To date, we have examined six of these jet fuel samples via ^{1}H and ^{13}C FT nmr. Representative ^{1}H and ^{13}C nmr spectra for the modified JP-4 (01) sample are presented in Figures 11 and 12. We anticipate complete ^{1}H and ^{13}C FT nmr analysis of the remaining samples (18) within the next two months. In the present report in view of the incomplete nmr data set, we will report only some of the cursory observations to date. In Table 3, aromaticity values obtained directly from ^{13}C spectra are compared with values obtained via the standard ASTM procedure. In several cases, the ASTM method yields higher aromaticity values than those obtained via the nmr approach.

In Figure 13, we report a tentative correlation between the observed freezing points of several fuels and average n-alkane length obtained directly from ^{13}C nmr spectral data. In the final report of this study a complete data set of the important molecular parameters obtained from the ^{1}H and ^{13}C FT nmr data such as total, aromatic and aliphatic hydrogen to carbon ratios, $(H/C)_{tot.}$, $(H/C)_{ar.}$ and $(H/C)_{al.}$, respectively, will be provided.

4. Exploration of Double Resonance NMR Techniques for Fuel Analysis

To date, we have not accomplished any of the work under this phase of the study. We anticipate a limited exploration of this work in the last two months of this one year study; however, a more detailed examination of this approach will be done in the second year of this contract.

Addendum:

1. Although not specifically mentioned in the present work plan, we have made considerable progress in developing a computer program to predict and quantify discrete components present in jet fuel mixtures utilizing ^{1}H and ^{13}C FT nmr data as input parameters.
2. I should also note that during the fall of 1978 we encountered major break-downs in the available FT nmr instrumentation. We have now repaired this instrumentation and the recent acquisition* of an additional nmr instrument will allow completion of this work on schedule.

*) I would like to express a sincere note of thanks to Dr. Bob Hazlett (NRL) for his gracious help in securing this equipment.

TABLE I

SYNTHETIC MIXTURES*

SYNTHETIC MIXTURE	1	2	3	4	5	6	7	8
AROMATICITY **	2%	9.5%	16.5%	17.5%	25.5%	30%	44.5%	80%
o-xylene	0.39	1.02	3.81	5.517	5.33	9.32	7.30	16.72
m-xylene	0.57	0.88	1.90	1.85	4.26	11.19	6.07	13.40
p-xylene	0.32	0.91	3.81	4.64	7.33	7.45	12.13	5.05
n-butyl benzene	0.28	1.25	1.62	1.18	3.19	1.19	7.67	8.46
tetralin	0.24	8.12	0.82	1.73	3.99	3.49	7.55	15.70
napthalene	0.34	0.47	3.84	4.02	5.15	2.25	5.85	20.23
benzene	0.24	0.708	2.49	1.70	1.98	2.75	8.92	18.61
n-nonane	18.60	17.93	23.02	5.62	18.66	11.25	10.24	0.39
isoctane	20.94	10.70	13.69	24.90	6.81	15.62	7.69	0.53
hexane	19.52	14.76	8.59	4.54	12.11	8.84	5.89	0.41
methyl cyclohexane	26.09	15.63	5.81	4.21	6.35	10.18	10.30	0.24
dodecane	12.43	27.63	30.59	40.10	24.78	16.47	10.38	0.27

* % of component by weight

** molar aromaticity

Table 2

Jet Fuel Samples and Source*

Sample #	
1	Sample VI/NR-77-01 Modified JP-4 This sample was blended especially for a combution test program, which had as its purpose the definition of fuel chemistry effects on engine performance. The basic JP-4 fuel was blended with a highly aromatic solvent (containing mainly xylenes) to give an aromatic content above 35%.
3	Sample VI/NR-77-03 JP-8 This sample is a baseline, unmodified JP-8 fuel used in a combustion test program conducted by one of the major engine manufacturers.
4	Sample VI/NR-77-04 Modified JP-8 This sample was blended for a combustion test program, to determine the effect of increased aromatics content on engine performance. The baseline JP-8 was blended with a highly aromatic solvent (primarily xylenes) to give an aromatic content above 35%.
5	Sample VI/NR-77-05 Modified JP-8 This sample was blended for a combustion test program by one of the major jet engine manufacturers. Purpose is to determine the effect of extending the boiling range of the fuel upon engine performance. The boiling range was extended by blending with about 12% of a paraffinic light mineral oil.
6	Sample VI/NR-77-06 Routine JP-7 Received from USAF quality control laboratory; represents a routine JP-7 procurement from a major refiner.
7	Sample VI/NR-77-07 Routine JP-7 Received from USAF quality control laboratory; represents a 383,000 gallon batch of JP-7 purchased from a major refiner.
8	Sample VI/NR-77-08 Experimental Fuel This is an experimental turbine engine fuel of uncertain history.

Sample#	
9	Sample VI/NR-77-09 <u>Routine Jet-A</u> Received from USAF quality control laboratory; represents a 45,000 gallon batch of Jet-A from a commercial refinery. (U.S. Air Force via A. Butler).
13	Sample VI/NR-77-13 <u>Routine JP-4</u> Received from USAF quality control laboratory; represents a 45,000 barrel batch of routine JP-4 purchased from a major refinery.
14	Sample VI/NR-77-14 <u>Routine JP-4</u> Received from USAF quality control laboratory; represents a 49,500 gallon batch of routine JP-4 purchased from a commercial source.
15	Sample VI/NR-77-15 <u>Routine JP-4</u> Received from USAF quality control laboratory; represents a 420,000 gallon batch of routine JP-4 purchased from a major refinery.
16	Sample VI/NR-77-16 <u>Routine JP-4</u> Received from USAF quality control laboratory; represents a 950,000 gallon batch of routine JP-4 purchased from a commercial supplier.

*) Samples I-I9 obtained from Dr. R. Butler, U.S.A.F.

Table 2 continued

2	VI/NR-77-02	Modified JP-8 (U.S. Air Force via Dr. Butler)
10	VI/NR-77-10	Specification JP-7 (U.S. Air Force via Dr. Butler)
11	VI/NR-77-11	Shale Oil JP-4 (U.S. Air Force via Dr. Butler)
12	VI/NR-77-12	Shale Oil Jet A (U.S. Air Force via Dr. Butler)
17	VI/NR-77-17	Specification JP-4 (U.S. Air Force via Dr. Butler)
18	VI/NR-77-18	Specification JP-4 (U.S. Air Force via Dr. Butler)
19	VI/NR-77-19	Specification JP-8 (U.S. Air Force via Dr. Butler
20	Shale Paraho	JP-5 (NRL via Dr. Hazlett)
21	Coal coed process	JP-5 (NRL via Dr. Hazlett)
22	NASA #4 Jet A Shale (TOSCO)	(NRL via Dr. Hazlett)
23	NASA #5 Jet A (H-Coal)	(NRL via Dr. Hazlett)
24	NASA #6 Jet A (H-Coal)	(NRL via Dr. Hazlett)

Table 3

FUEL AROMATICITY (F_A)

SAMPLES	F_A(NMR) %	F_A(ASTM) %
JP-4(15)	6.9	8.2
modified JP-8(05)	7.8	16.0
JP-8(03)	8.8	15.2
COED 5	15.8	25.0
SHALE PARAHO	17.2	26.0
modified JP-4(01)	37.2	38.9

Figure Captions

Figure 1 - Chromatogram of JP-4 (15) and JP-4 (01) jet fuels R.I. detector on SX-8 Biobeads gel permeation column, 50 cm column, 0.5 cm diameter, and flow rate of 2ml/min. Solvent was THF.

Figure 2 - Chromatogram of JP-8(03) and JP(05) jet fuels R. I. detector on SX-8 Biobeads gel permeation column, 50 cm column, 015 cm diameter, and flow rate of 2ml/min. Solvent was THF.

Figure 3 - Aromaticity data for synthetic models via ASTM (1319-77).

Figure 4 - Freezing point data for synthetic models via ASTM (2386-67).

Figure 5 - Aromaticity data for JP-4 jet fuels via ASTM (1319-77).

Figure 6 - Aromaticity data for JP-7 and JP-8 jet fuels via ASTM (1319-77).

Figure 7 - Aromaticity data for JP-7 and JP-8 alternate energy jet fuels via ASTM (1319-77).

Figure 8 - Freezing point data for JP-4 jet fuels via ASTM (2386-67).

Figure 9 - Freezing point data for JP-7 and JP-8 jet fuels via ASTM(2386-67).

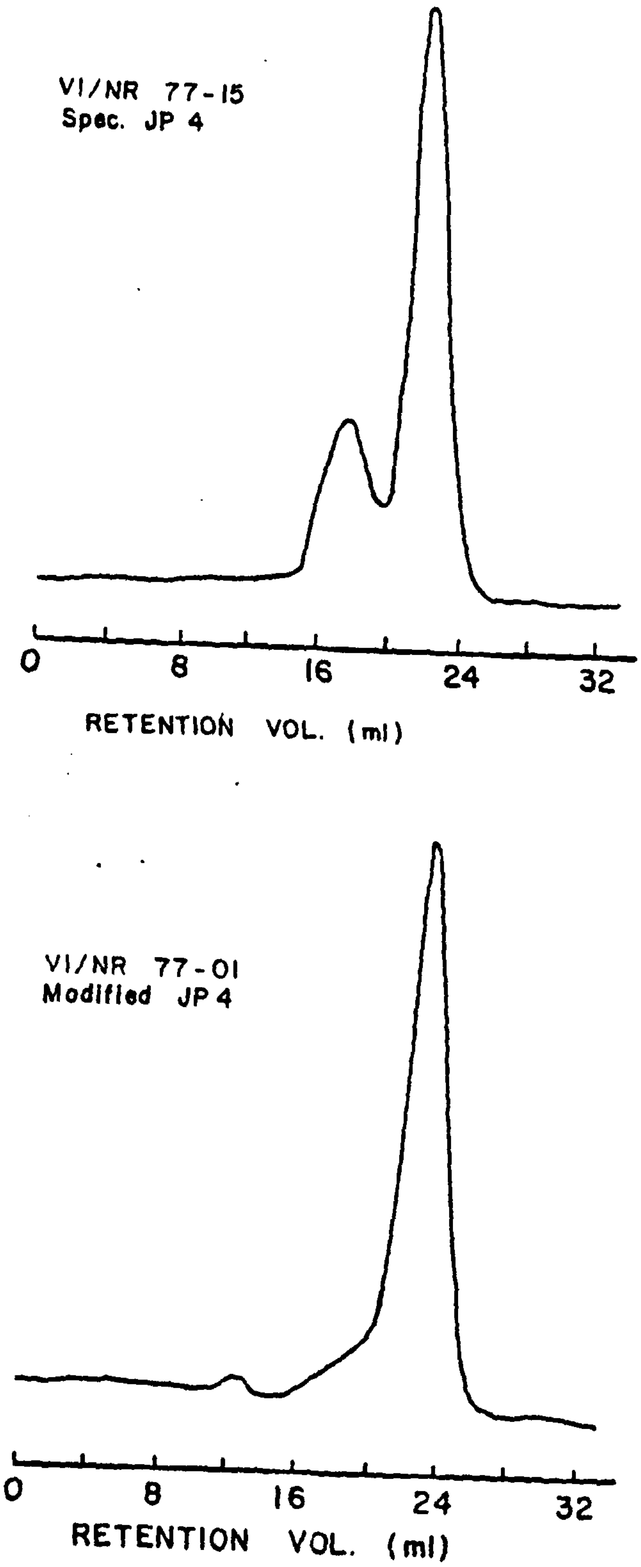
Figure 10 -Freezing point data for alternate energy jet fuels via ASTM (2386-67).

Figure 11 -'HFT NMR spectrum of JP-4(01) sample in $DCCl_3$ with hexamethyl disiloxane quantitative reference, (0.0ppm).

Figure 12 -^{13}C FT NMR spectrum of JP-4(01) sample in $DCCl_3$ with hexamethyl disiloxane quantitative reference (0.0 ppm).

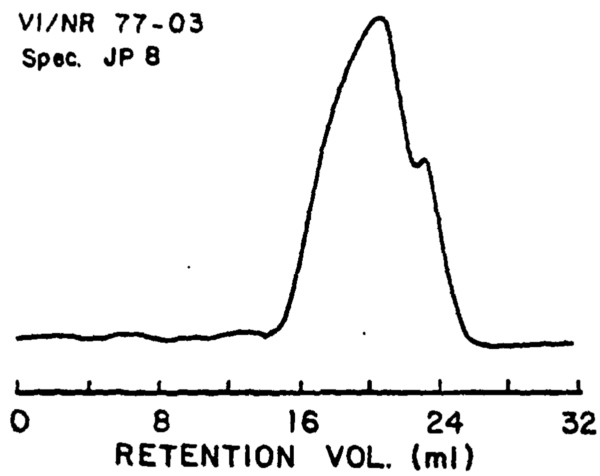
Figure 13 -Jet fuel freezing point correlation with average n-alkane length via ^{13}C nmr.

Figure 1



VI/NR 77-15
Spec. JP 4
0
8
16
24
32
RETENTION VOL. (ml)
VI/NR 77-01
Modified JP 4
0
8
16
24
32
RETENTION VOL. (ml)

Figure 2


VI/NR 77-03
Spec. JP 8
0
8
16
24
32
RETENTION VOL. (ml)

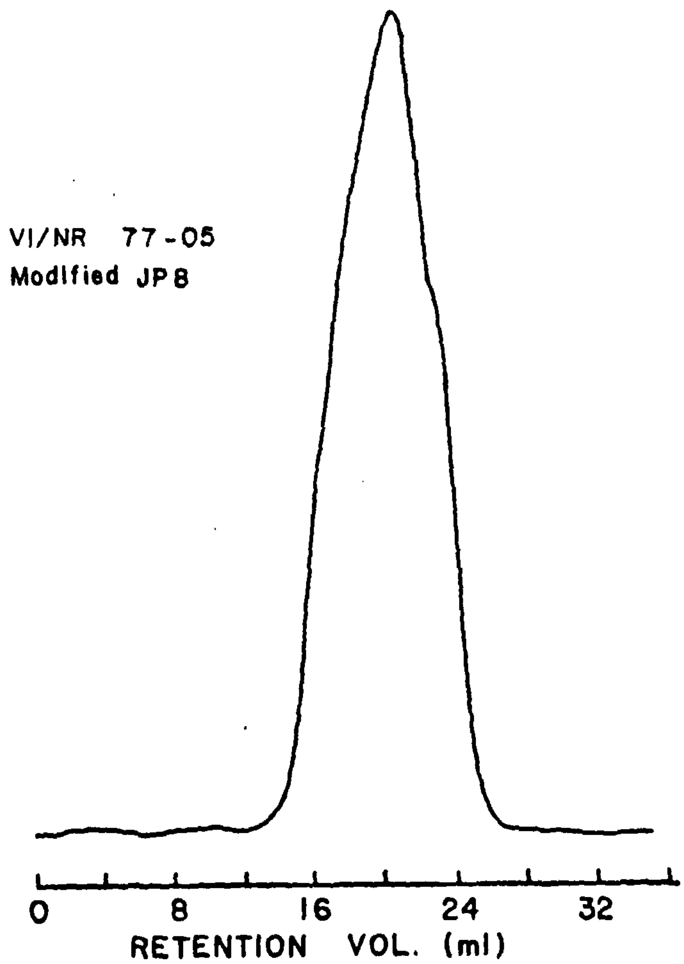

VI/NR 77-05
Modified JP8
0
8
16
24
32
RETENTION VOL. (ml)

Figure 3

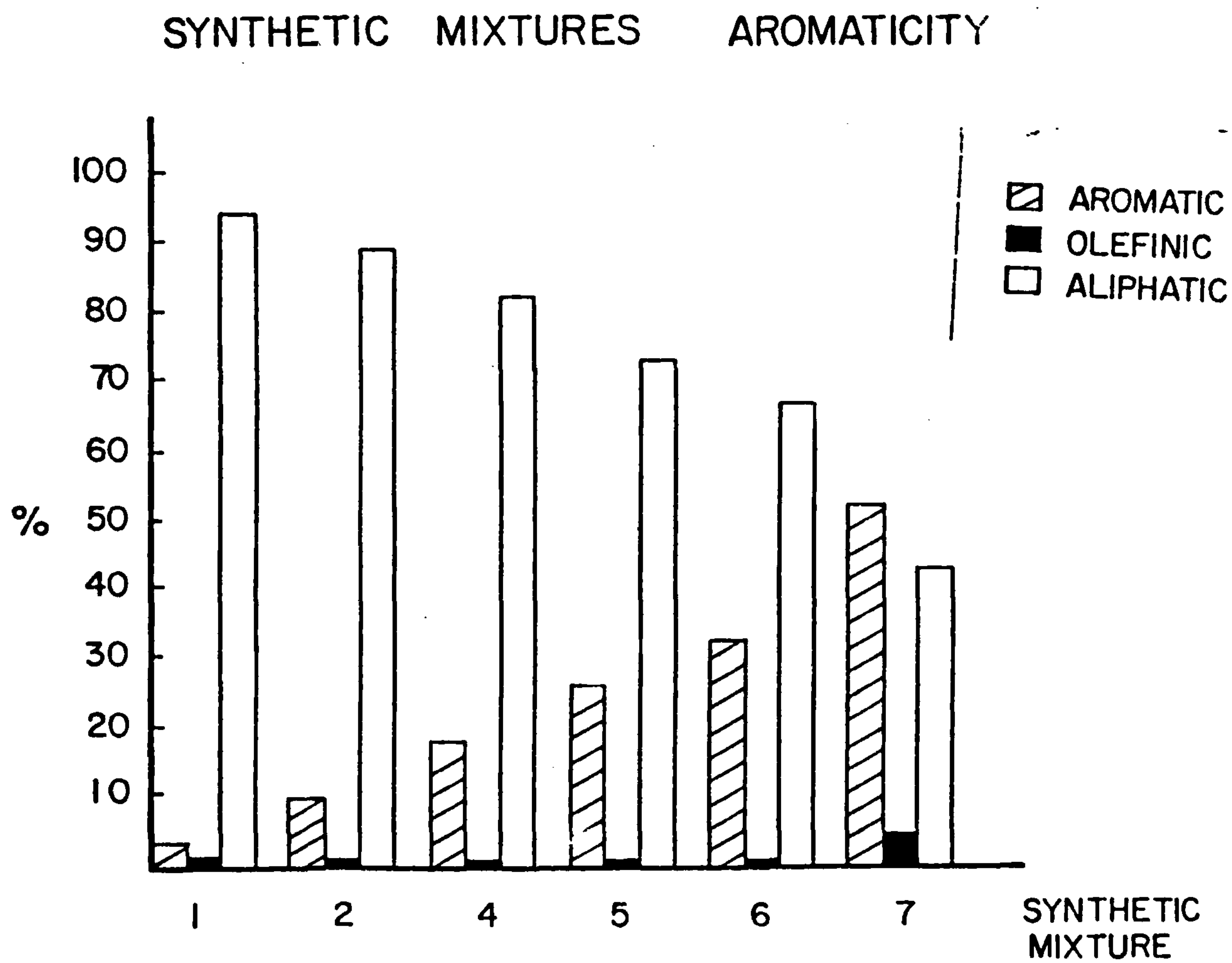

SYNTHETIC MIXTURES AROMATICITY
AROMATIC
OLEFINIC
ALIPHATIC
%
100
90
80
70
60
50
40
30
20
10
1
2
4
5
6
7
SYNTHETIC MIXTURE

Figure 4

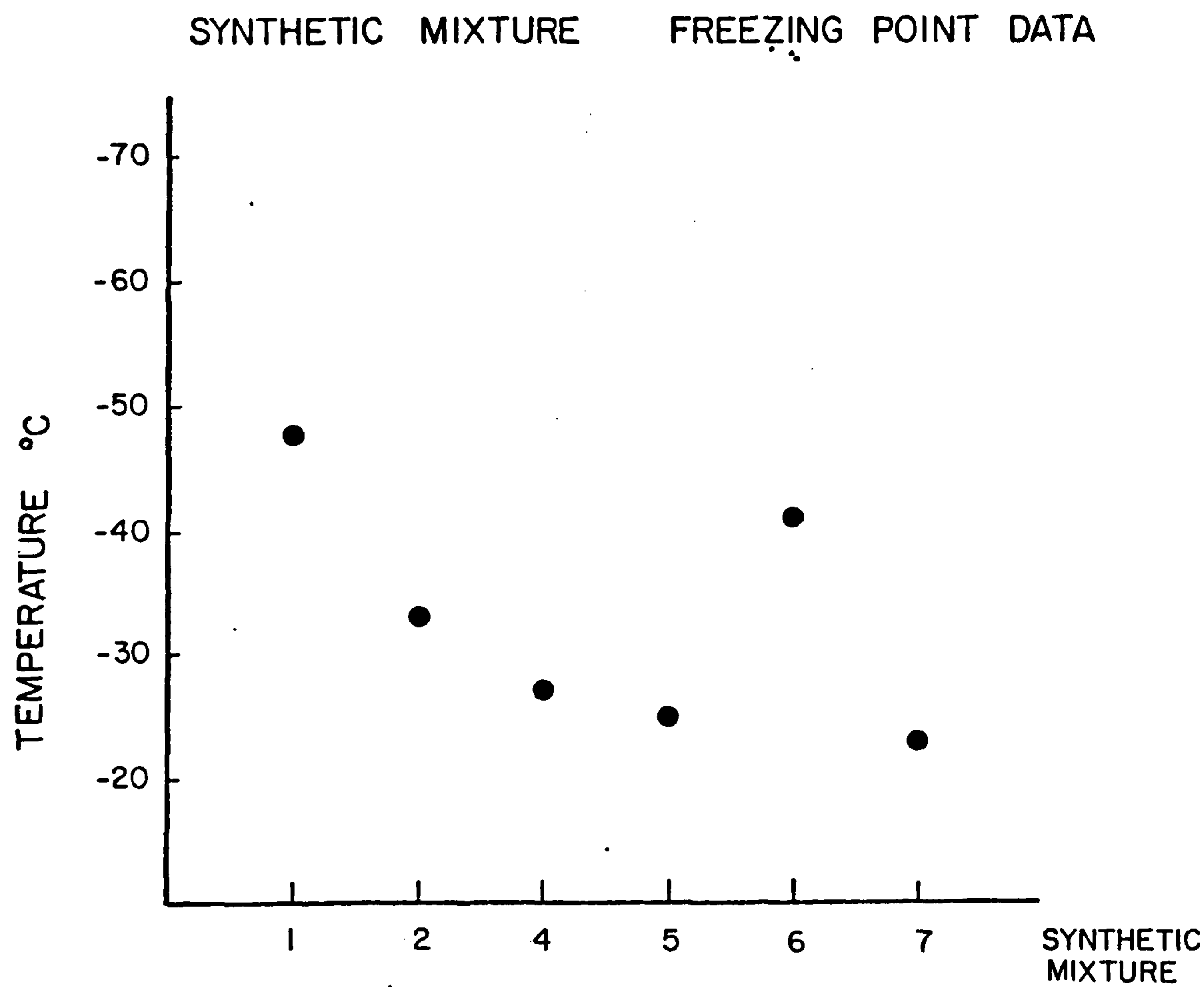
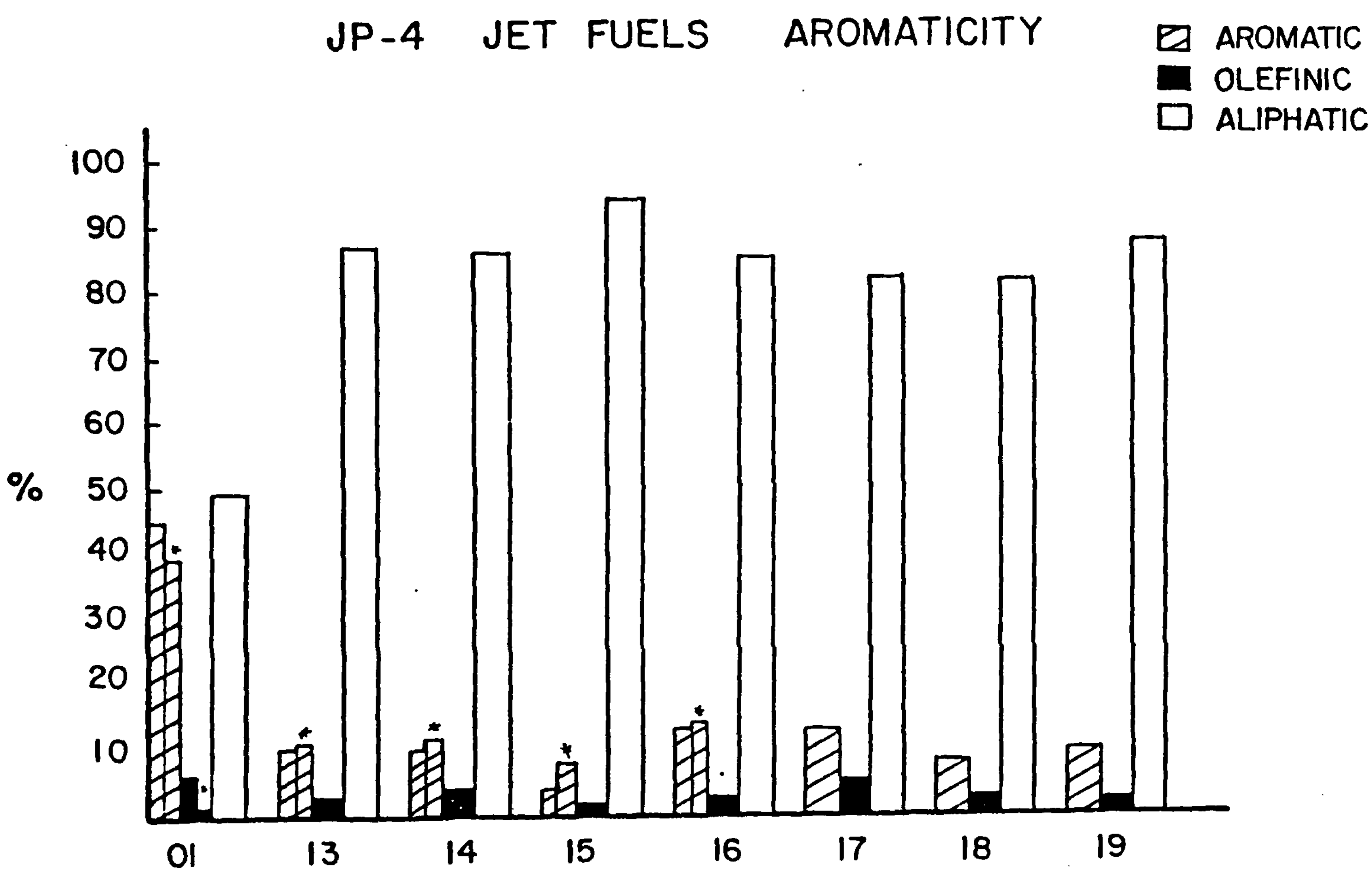
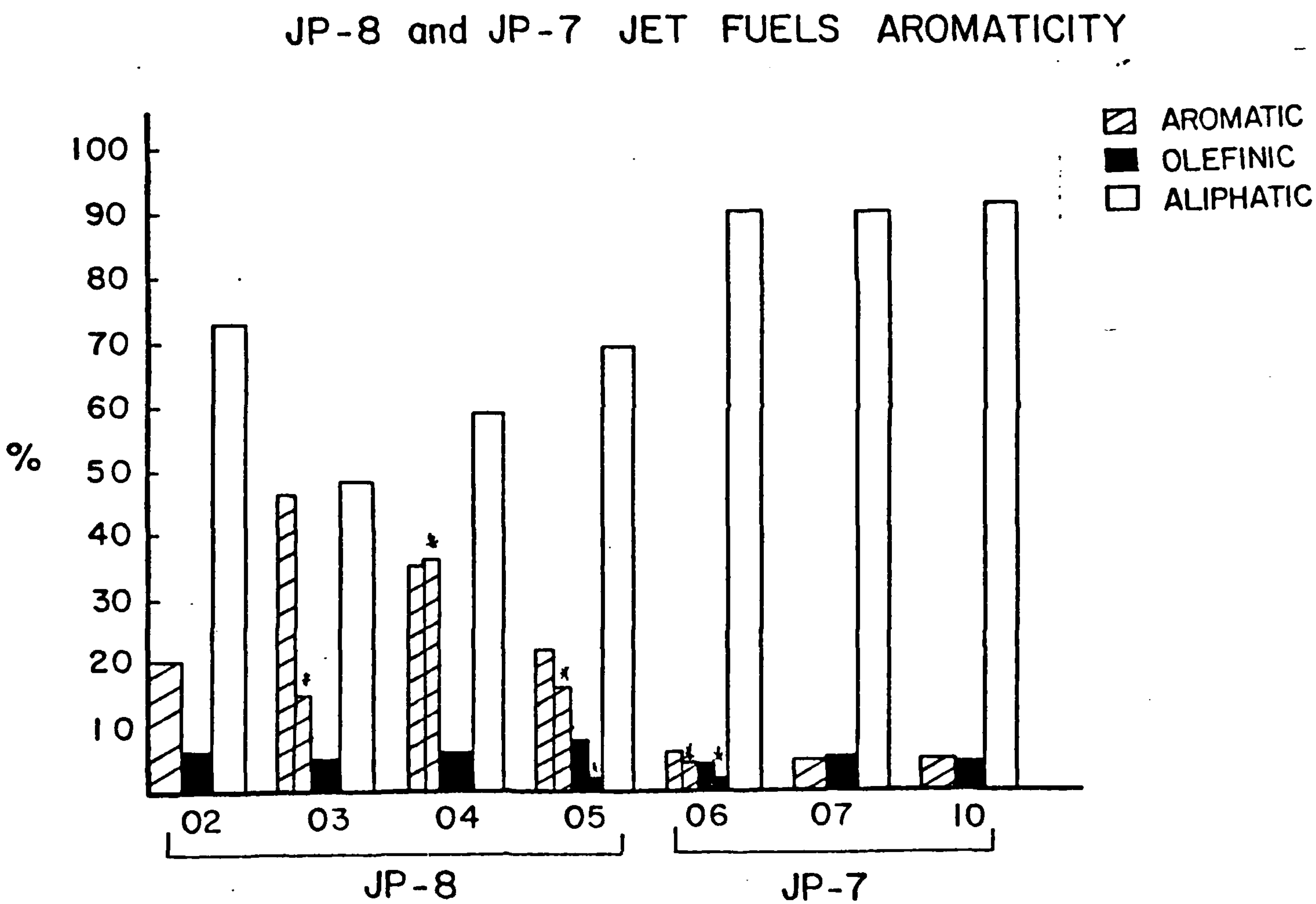

SYNTHETIC MIXTURE FREEZING POINT DATA
TEMPERATURE °C
-70
-60
-50
-40
-30
-20
1
2
4
5
6
7
SYNTHETIC MIXTURE

Figure 5



*) Values provided on data sheets for these samples via Dr. Butler.

Figure 6



*) Values provided on data sheets for these samples via Dr. Butler.

Figure 7

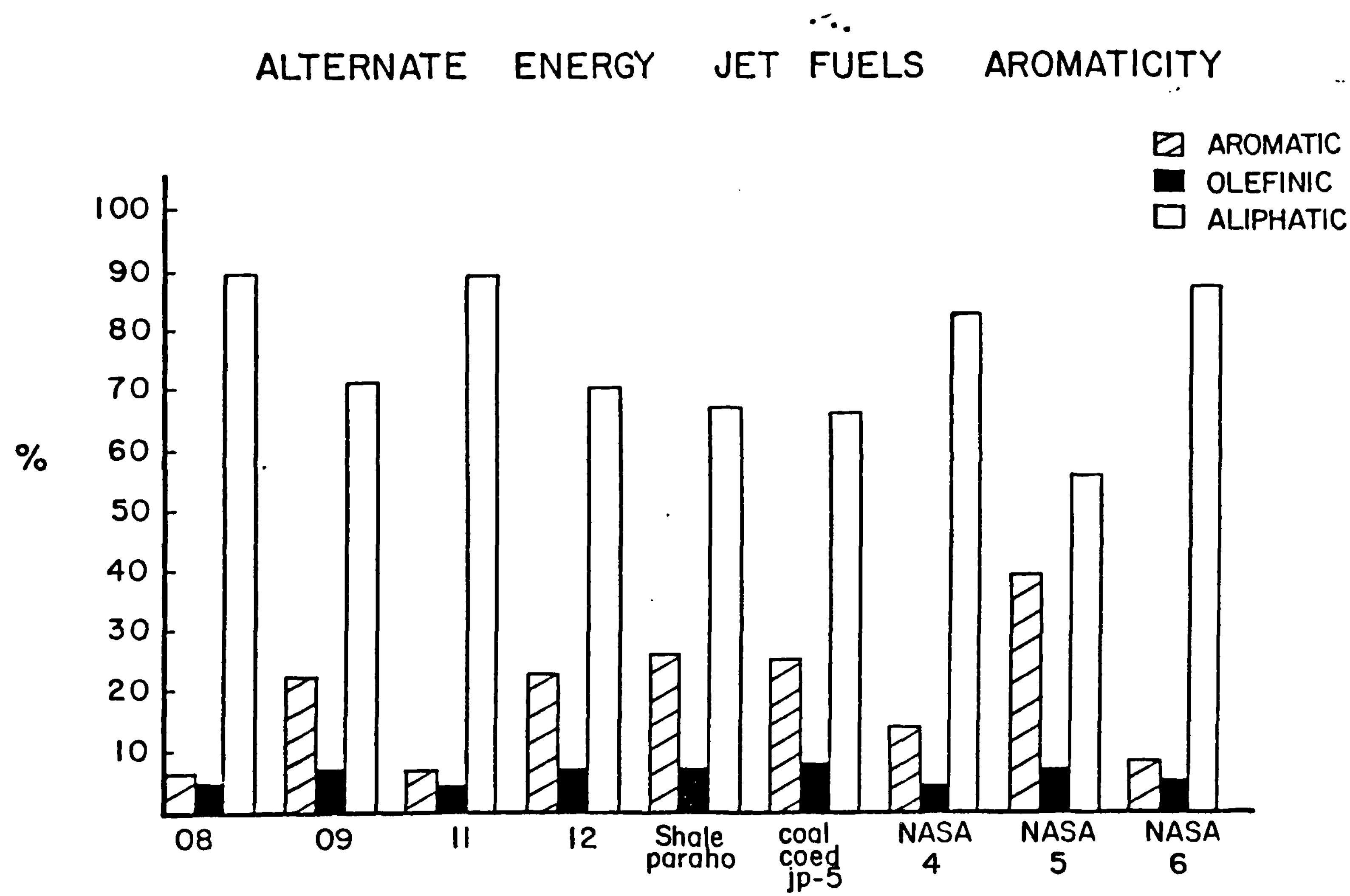

ALTERNATE ENERGY JET FUELS AROMATICITY
AROMATIC
OLEFINIC
ALIPHATIC
%
100
90
80
70
60
50
40
30
20
10
08
09
11
12
Shale paraho
coal coed jp-5
NASA 4
NASA 5
NASA 6

Figure 8

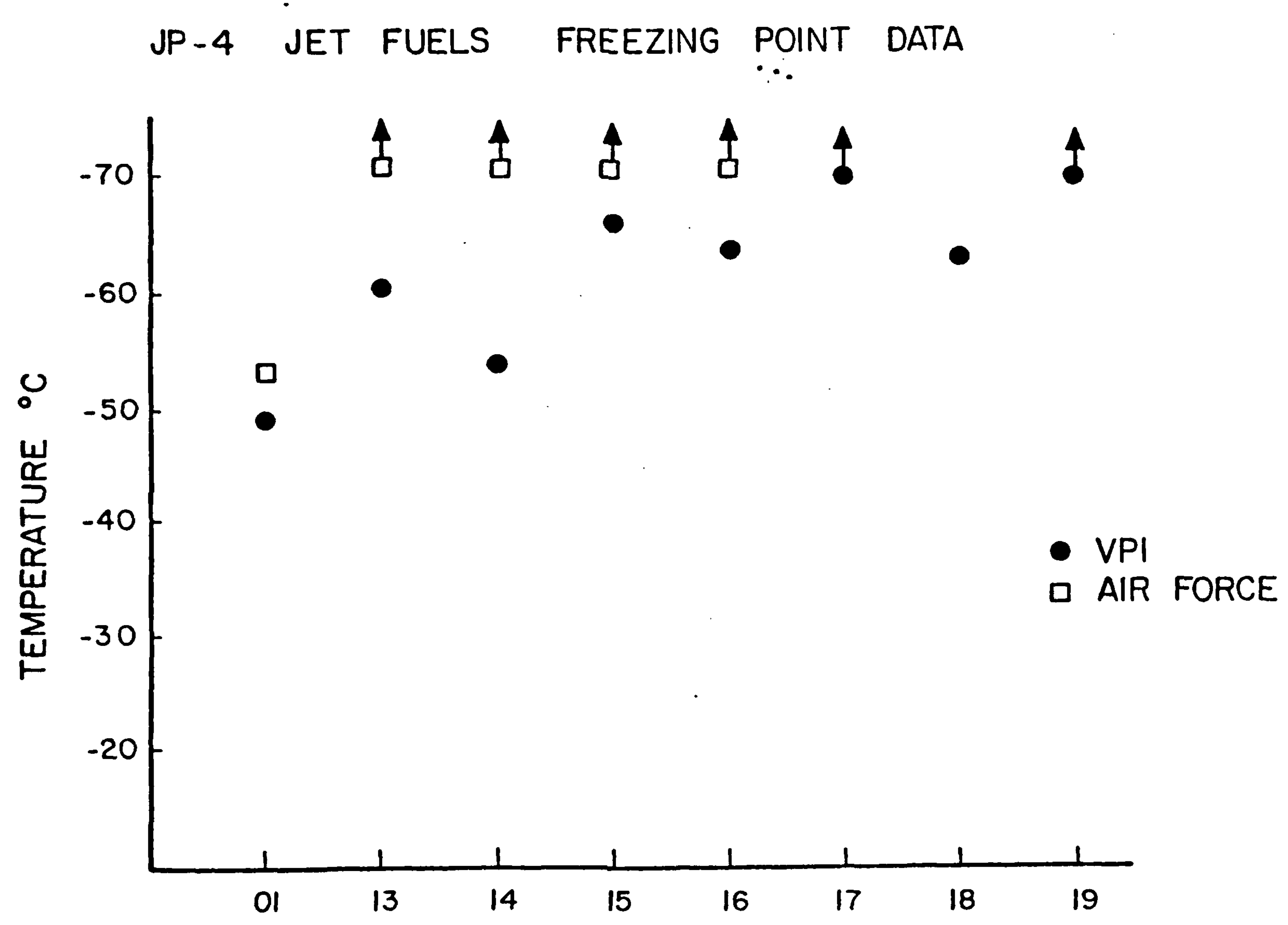

JP-4 JET FUELS FREEZING POINT DATA
TEMPERATURE °C
-70
-60
-50
-40
-30
-20
01
13
14
15
16
17
18
19
VPI
AIR FORCE

Figure 9

JP-8 and JP-7 JET FUELS FREEZING POINT DATA

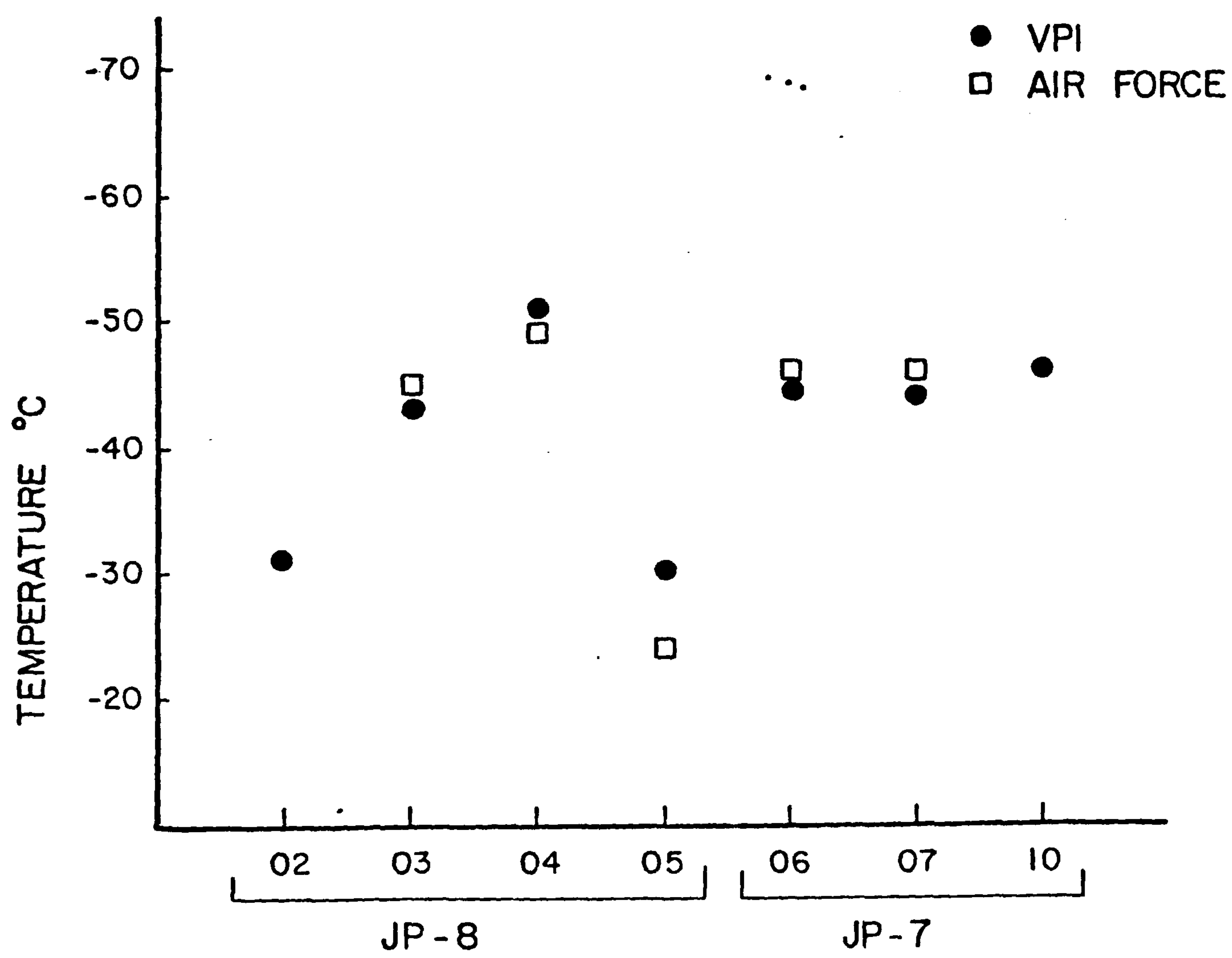
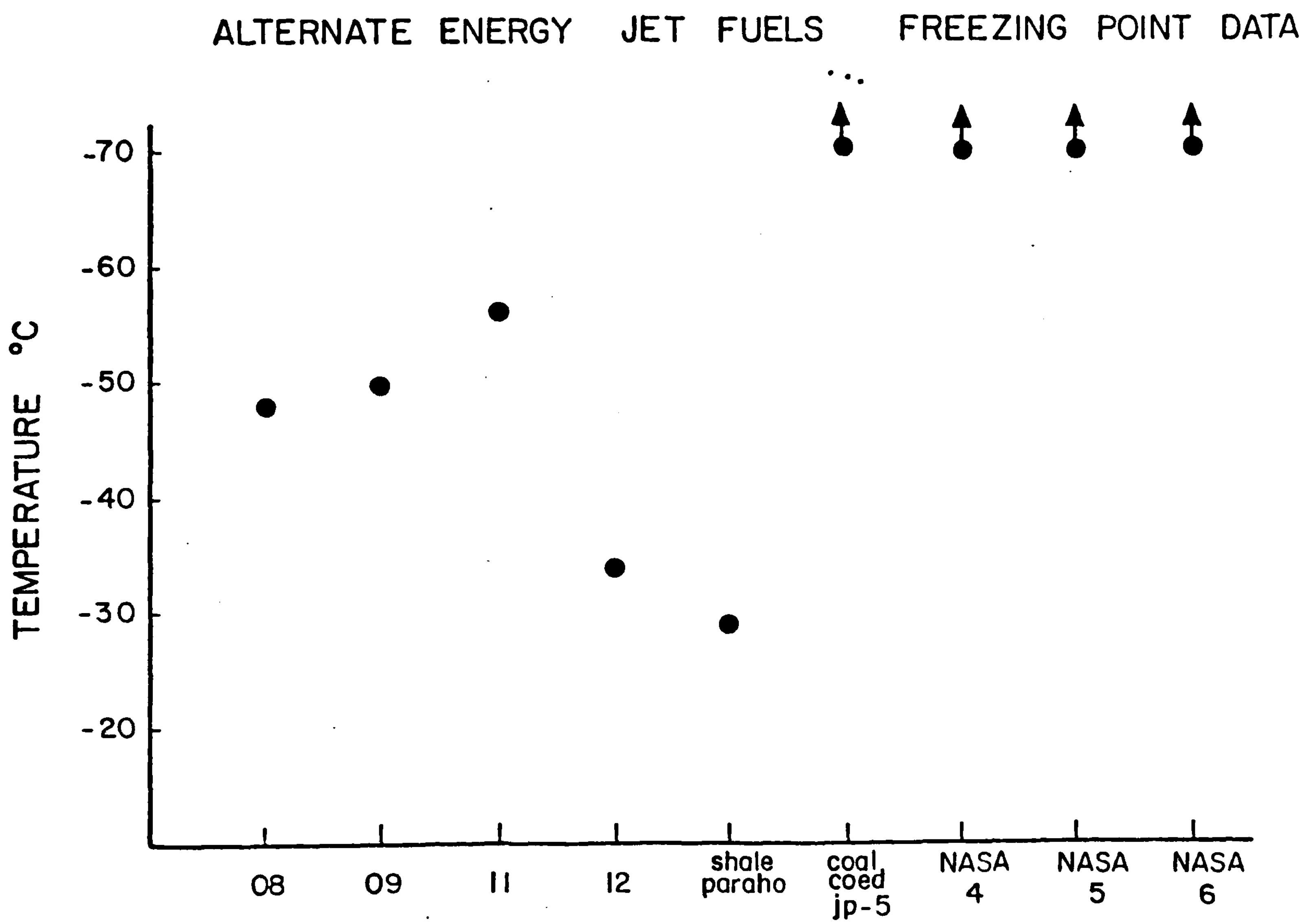
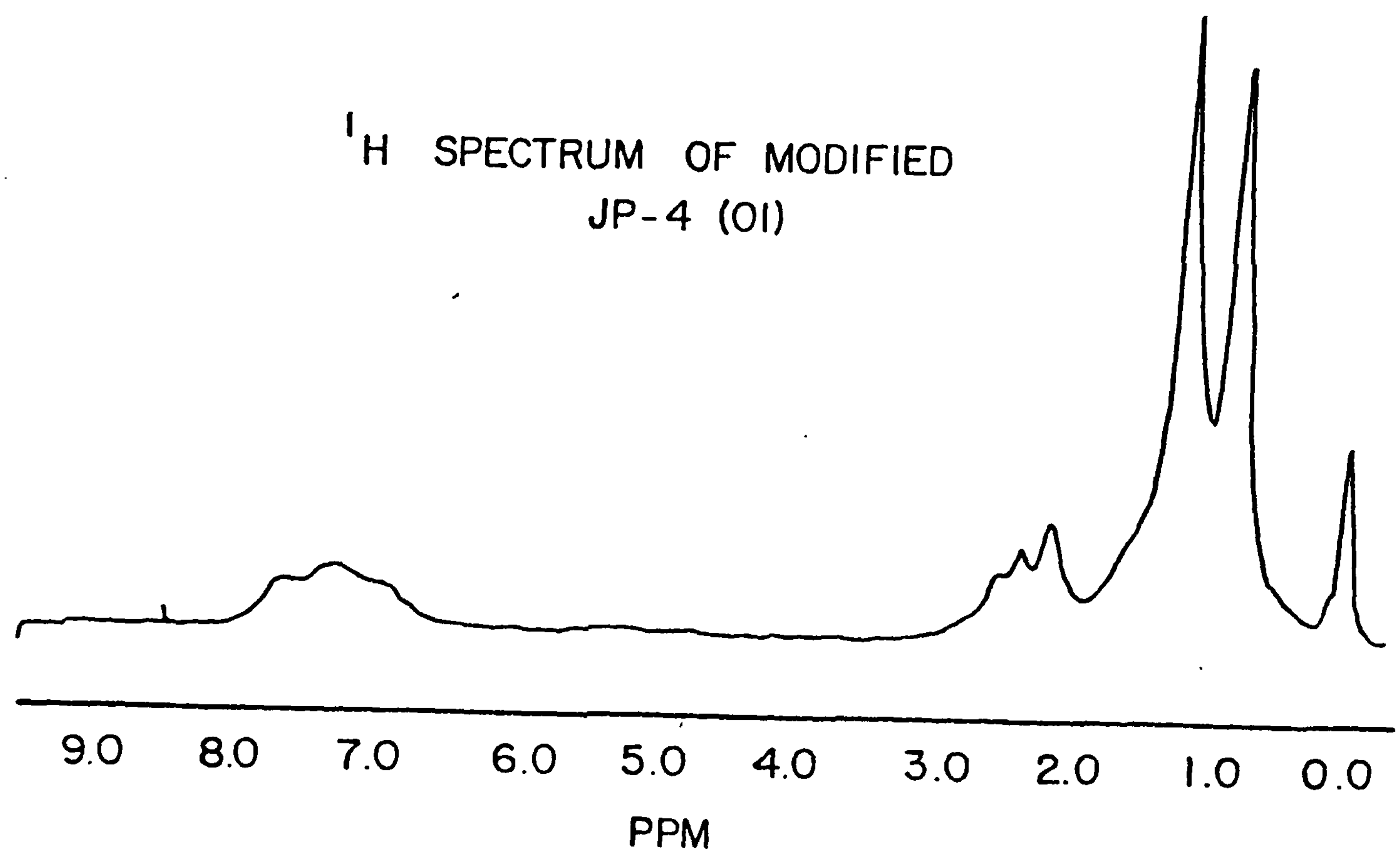


Figure 10



ALTERNATE ENERGY JET FUELS FREEZING POINT DATA
TEMPERATURE °C
-70
-60
-50
-40
-30
-20
08
09
11
12
shale paraho
coal coed jp-5
NASA 4
NASA 5
NASA 6

Figure 11



LC-^{1}HNMR: Model Study and Application to Petroleum and Synthetic Fuels Using Continuous Flow ^{1}H NMR

by

James F. Haw, T. E. Glass, D. W. Hausler, E. Motell,[1] and H. C. Dorn*

Department of Chemistry
Virginia Polytechnic Institute
and State University
Blacksburg, VA 24061

[1]Visiting Professor, Department of Chemistry, San Francisco State University

BRIEF

The performance of a liquid chromatograph directly coupled to a ^{1}H NMR detector (LC-^{1}HNMR) is described. Results obtained for a simple mixture and several jet fuels illustrate the utility of this approach.

ABSTRACT

Initial results obtained for a flow ^{1}H NMR detector directly coupled to a liquid chromatography unit are described. Results achieved for a model mixture and several jet fuel samples are discussed. The limitations and advantages of this liquid chromatography detector are compared with more commonly employed detectors, (e.g., refractive index detectors).

INTRODUCTION

The widespread applicability of high performance liquid chromatography (HPLC) for separation of complex mixtures is well recognized. Although a number of different detectors (e.g., refractive index, u.v., etc.) are commonly employed in high performance liquid chromatography, most of these are nonselective for discrete compound identification. A possible exception is the Fourier Transform Infrared detector for liquid chromatography.[1]

Fourier transform nuclear magnetic resonance (FT-NMR) is a proven technique for spectral analysis of pure compounds and simple mixtures. In addition, the relatively high NMR sensitivity of the ^1H nuclide is attractive for applications requiring limited sample and/or "available time window" for spectroscopic examination. The latter requirements characterize the initial requirements for a continuous flow detector in high performance liquid chromatography utilizing ^1H NMR as the detector (LC-^{1}HNMR). Non chromatographic applications of flow NMR have previously been reported. Rapid irreversible chemical reactions as well as transient phenomena such as CIDNIP have been studied by stopped-flow NMR.[2] The theoretical formalism for the study of fast transient chemical reactions by FT-NMR has also been reported.[3] An apparatus for continuous-flow FT-NMR has previously been described by Fyfe et.al.[4] The effect of line broadening due to decreasing residence time with increasing flow rates was discussed. A value of $T_{2(OBS)}$ (observed spin-spin relaxation time) for varying flow rates is defined in the equation below.

$$1/T_{2(OBS)} = (1/T_{2(STAT)}) + (1/\tau)$$

The spin-spin relaxation time ($T_{2(STAT)}$) is the value for static samples and τ is the residence time in the receiver coil (related to flow rate). An analogous expression can be written for the observed value for spin-lattice relaxation times.

Another obvious consideration in LC-NMR is solvent selection, but this is also an important consideration with virtually every LC detector. Freon 113 (1,1,2 trifluoro-trichloroethane), deutero-chloroform and carbon disulfide are possible solvent candidates which span a fairly wide polarity range. Although perhaps too expensive to use neat (even with recycle), d_4-methanol could serve as a polar modifier at the several percent level. All separations involving deuterated solvents can be optimized with the cheaper protonated analogues prior to LC-^{1}HNMR analysis. Chemical shift references such as TMS may be added directly to the mobile phase with neglible effect upon elution characteristics so long as the reference does not strongly interact with the stationary phase. Similarly, quantitative references may also be added. The extension of this technique to ^{19}F FT NMR analysis of fluorinated derivatives is not resticted by detector considerations. In general, the solvents that are suitable for LC-^{1}HNMR have reasonable spectral windows for LC-FT-IR. The two techniques could easily provide complimentary information.

Obviously, one of the major advantages of the LC-^{1}HNMR approach is the saving in sample manipulation and analysis time. This is particularity valid when compared with the tedious process of

individual chromatographic fraction collection, solvent evaporation, and preparation for static NMR or other spectroscopic examination. Recently, a liquid chromatography effluent stream coupled to a ^{1}H NMR spectrometer has been described for static examination of chromatographic fractions.[5] We believe that our work is the first description of a continuous flow LC-^{1}HNMR system.

In this paper, we report the design of our LC-^{1}HNMR insert and present the results for a typical model mixture to demonstrate the advantages of this technique. A simple mixture of four different hydrocarbons was first examined. In addition, four experimental military jet fuels were studied, since they represent relatively complex mixtures amenable to the LC-^{1}HNMR approach.

Experimental

The jet fuel samples were supplied by the Air Force Aero Propulsion Laboratory (Wright-Patterson Air Force Base, Ohio) and the Naval Research Laboratory (Washington, D.C.). The four jet fuels used in this study were: a routine JP-4; a modified JP-4 (sample modified by adding xylenes and naphthalenes); a Shale Paraho JP-5, and Coal Coed process JP-5. The latter two samples are experimental fuels derived from shale and coal, respectively. The model mixture sample was prepared by mixing: 1.00 g. isooctane, 1.00 g. 2-hexene, 1.25 g. benzene, and 1.00 g. naphthalene. Trichlorotrifluoroethane (Miller-Stephenson Chemical Co.) was degased prior to use as the chromatographic solvent. Enough tetramethylsilane (TMS) was added to the solvent after degasing to make it $\sim$0.3% by volume.

A Merk Silica Gel 60 Size B (310mm x 25mm I.D.) column was used after solvent equilibration. The pump was a Waters M-45 solvent delivery system. A Valco injection valve with a 500μl sample loop was used throughout. All samples were injected neat. A Laboratory Data Control Model 1107 refractive index detector was used to obtain classical chromatograms. The NMR flow cell was connected directly to the outlet of the RI detector via a length of teflon tubing. The lag time between the RI detector and the NMR receiver coil was determined to be 40 sec at a flow rate of 2.5ml/min. Effluent was removed from the NMR flow cell through a teflon tube and into a cold trap by a vacuum pump.

A Jeolco PS-100 nuclear magnetic resonance spectrometer was used to obtain ^{1}H spectra at 100.0 MHz for the flow studies. The spectrometer was used in the Fourier Transform (FT) mode with a Digilab Data System. A fixed head 128K Alpha Data Disc allowed sufficient data storage for 42 (2048 point) spectral files and required a minimum of 110 msec for each spectral file transfer from the computer (Nova 1200). Figure 1 is a schematic diagram of the ^{1}HNMR insert used in these LC-^{1}HNMR studies. The spectrometer was operated with an external proton lock system. The comparison ^{1}HNMR spectra of the jet fuels were obtained at 90.0 MHz in the CW mode utilizing a Varian EM-390 spectrometer. Hexamethyldisiloxane was used as the reference and lock signal.

RESULTS AND DISCUSSION

The four component model mixture have an elution order of isooctane, 2-hexene, benzene and naphthalene, respectively, utilizing

the chromatographic conditions described in the Experimental Section. The normal Refractive Index (RI) trace obtained for this mixture is presented in Figure 2a. Good resolution is indicated in spite of relatively high sample loading. This is also indicated in Figure 3 which is the LC-^{1}HNMR profile obtained for this chromatographic run. Spectra with no peaks other than the reference TMS have been omitted. The growth and decay of compounds as one examines progressively later spectra is readily apparent.

Figure 4 shows spectra selected from near the maxima of the four chromatographic peaks. Resolution and sensitivity may be more readily evaluated in this figure than in the stacked plot. Although line widths of 6-7 Hz were typically obtained, line widths of 5 Hz were the best that could be obtained with our present insert. Since Fyfe [4] was able to do considerably better with similar conditions, a considerable improvement in resolution is certainly feasible with improved receiver insert design. Given our 5 Hz limitation on magnet inhomogeneity, an acquisition time of 0.4 sec was selected as a compromise between sensitivity and further degradation of line widths. Doubling the flow rate (2.5 to 5 ml/min) did not substantially degrade resolution so the line width contribution from residence time was minor under these conditions.

It must be emphasized that very little has been done to optimize flow cell design or the receiver coil configuration. More careful cell design should substantially improve resolution and sensitivity. Since each file spectrum is collected under identical conditions,

integrals from a given spectrum should be directly comparable with those obtained from other spectral files within the same chromatographic data set. This is apparent in the relatively constant amplitude for the TMS peak in Figure 3 from file to file. Ideally, one could compute all integrals relative to a quantitative standard (something less volatile than TMS such as hexamethyl disiloxane would be preferable) present in the mobile phase. In any event, each spectrum in a set may be integrated and plotted versus elution volume to give a proton response chromatogram, a "protonogram". The protonogram for the model mixture is presented in Figure 2b. This plot was constructed by integrating all peaks (exclusive of TMS) in each spectrum and plotting the total versus file (spectrum) number. The protonogram shows resolution that is very similar to that in the RI trace, demonstrating that under these conditions the dead volume between the RI detector and the NMR receiver coil is negligble. It should be noted that the sharp isooctane peak is underdetermined by the data points whereas an excessive number of spectra have been taken across the later eluting, broader naphthalene peak. Ideally spectra should be acquired very frequently early in the chromatogram (where higher concentration permits fewer transients to be taken), and spectra should be taken infrequently across later eluting peaks where collecting more transients becomes important. Since peak width is (ideally) related linearly to elution volume, the number of transients per spectrum could be increased linearly.

If one integrates a protonagram peak and corrects for the number of protons per molecule, a molar response is obtained. Based on the known composition of the model mixture, the area of the benzene peak should be 1.54 times that of the naphthalene peak. A value of 1.50 was obtained from the protonogram. Given the line-widths with the present instrumentation and the normal proton chemical shift range, there are approximately 150 spectral channels of information presently available. In principle, protonograms could be constructed for each channel, producing "chromatograms" very specific for certain structural features (e.g., aromatic hydrogen).

Based on dilute model studies, we estimate ultimate detection limits of less than 1 μg for typical molecules (100-300 M.W.) for 10 second observation times.

Jet Fuels

The LC-^{1}HNMR profile for the paraho shale jet fuel (JP-5) is presented in Figure 5. The spectrum for the original jet fuel mixture yields considerably less information (Figure 6) with respect to the individual compounds present. The spectra for the alkanes (files 5-12) do not indicate the presence of branched hydrocarbons (no methine shoulder ~1.5 ppm). It is, therefore, reasonable to conclude that all of the aliphatic compounds in this sample are linear alkanes. If one assumes that each compound eluting under this envelope has two methyl groups, the number of methylene groups may be calculated from the ratio of the methyl and methylene peak integrals. The resulting trend is presented in Figure 7. Files

7 through 12 suggest a steady progression from n-decane to n-hexane. Elution volumes of standard samples run under identical conditions confirm this order. The ratios from files 5 and 6 are anomolous but could be rationalized as a frontal phenomena due to column overloading.

The aromatic envelope in the paraho shale oil sample contains 26% of the material by volume (ANSI/ASTM D 1319-77). The various compounds in this envelope elute over a broad range so the concentrations are relatively low. The signal to noise ratio for spectra of the aromatic envelope is, therefore, considerably less than that for the aliphatic envelope. Several generalizations can be made regarding the compounds present in this portion of the profile. Simple alkylbenzenes with short alkyl groups predominate early in the peak with a progression through the xylenes towards mesitylene with possibly some tetra and penta methyl benzene (files 34-37).

Again with coal COED JP-5, one can gather little information from the NMR spectrum prior to separation. Figure 8 is the LC-^{1}HNMR profile for this fuel. This coal-derived material contains highly branched aliphatic compounds. This is indicated by the high methyl/methylene peak ratio and obvious methine shoulder (~1.5 ppm). This high degree of branching is in sharp contrast to the linear alkane content found in the paraho shale oil derived fuel.

Files taken early on the aromatic peak of coal COED JP-5 show a preponderance of simple alkylbenzenes, xylene and possibly mesitylene. As more of the aromatic peak elutes, a progression

toward more highly methylated benzenes and possibly tetralin is observed.

The LC-^{1}HNMR profile for the routine petroleum derived jet fuel (JP-4) is presented in Figure 9. For comparison, the LC-^{1}HNMR profile for the modified (modified by addition of aromatics, e.g., xylenes and naphthalene derivatives) JP-4 sample is presented in Figure 10. The spectra for the alkane region files 6-11,(Figures 9 and 10) of these fuels are very similar with increasing alkyl branching indicated at later elution files (9-11).

The aromatic region for the routine JP-4 (Figure 9) indicates the trend from simple alkyl aromatics (possibly ethyl and propyl) to a predominace of xylenes. By comparison, the modified JP-4 Figure 10 clearly suggests the presence of 1- and 2-methylnapthalene. The RI trace (Figure 11) also indicates a large peak at an elution volume typical for naphthalene.

CONCLUSION

It is clear from the LC-^{1}HNMR results presented for the four different jet fuels that significant differences in sample composition are readily dessemible by this approach. That is, the LC-^{1}HNMR technique provides unique "fingerprints" for each jet fuel. For example, the clear differentiation of branched alkane from linear alkane content is readily apparent in the LC-^{1}HNMR results for these fuels whereas, the RI detector indicated only one peak. Although greatly limited by sensitivity relative to most LC detectors, flow LC-NMR generates a great deal of structural information quickly and conveniently. In cases where high resolution

and sensitivity are necessary, flow LC-NMR could still be used to screen effluents to identify fractions for conventional NMR analysis. In the extension of this technique to chromatographic columns of higher efficiency, lower sample capacity will tend to reduce sensitivity, but LC-^{1}HNMR detection cells matched to smaller sample volume would minimize peak broadening.

A second and perhaps more severe limitation of the LC-NMR approach is the limited choice of chromatographic solvents. However, the use of fluorinated and deuterated solvents is an obvious method of handling this limitation. In addition, saturation and/or double resonance NMR techniques could be useful when hydrogen containing solvents cannot be avoided.

Acknowledgement:

We wish to express our appreciation to the U.S. Air Force and Naval Research Laboratory for support of this work.

REFERENCES

1. D. W. Vidrine and D. R. Mattson, App. Spec. 32, 502 (1978).
2. J. J. Grimaldi, J. Baldo, C. McMurray, and B. Sykes, J. Am. Chem. Soc., 94, 7641 (1972).
3. R. Kühne, T. Schaffhauser, A. Wokaun, and R. Ernst, J. Mag. Res. 35, 39-67 (1979).
4. C. A. Fyfe, M. Cocivera, S. W. H. Damji, T. A. Hostetter, D. Sproat, and J. O'Brien, J. Mag. Res. 23, 377-384 (1976).
5. N. Watanabe and E. Niki, Proc. Jap. Acad., 54, 194-199 (1978).

Figure Captions

1. Diagram of LC-^{1}HNMR insert. The sample is polarized in region one (within magnetic field) and free induction decays are monitored in region two.

2a. Refractive index trace of model mixture.
 b. Plot of proton integrals versus file number (protonogram) for model mixture.

3. LC-^{1}HNMR profile for model mixture. Each file consists of 110 scans (0.4 sec acquistion time, 2K data points) or ~65 sec per file.

4. Selected spectra of each of the four model compounds near maximum model concentration on the LC-^{1}HNMR profile.

5. LC-^{1}HNMR profile for Paraho Shale Jet Fuel JP-5 (spectral conditions same as indicated in Figure 3).

6. ^{1}HFTNMR Spectrum for total Paraho Shale JP-5 mixture at 90 MHz. This sample contains tris(acetylacetonato) chromiumIII quantitative measurements (resolution intentionally degraded for comparative purposes with LC-^{1}HNMR profile)(Figure 5).

7. Correlation between average n-alkane chain length versus file number for aliphatic peak of Paraho Shale Jet Fuel JP-5.

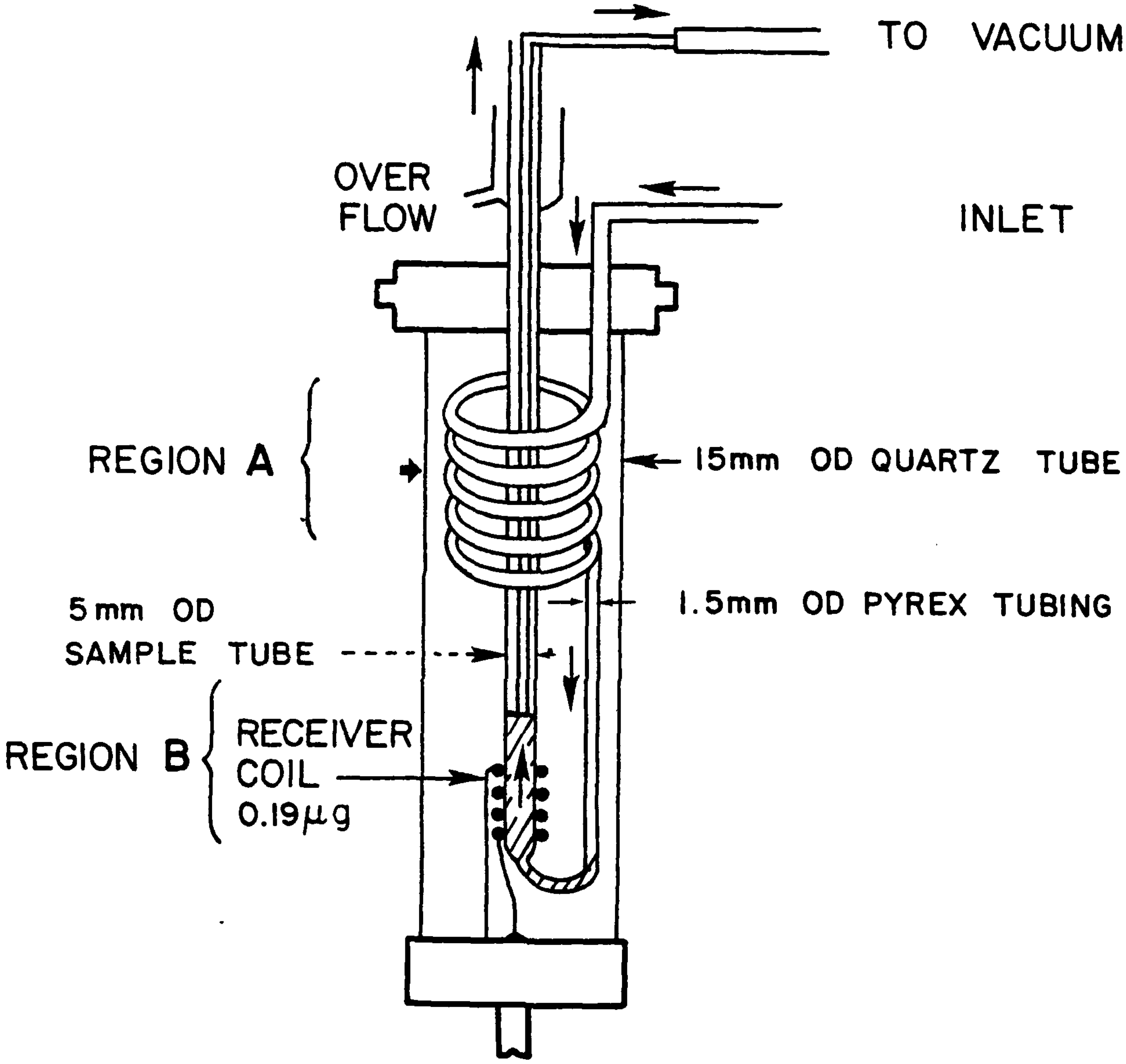
8. LC-^{1}HNMR profile for Coal Coed Jet Fuel JP-5 (spectral conditions same as indicated in Figure 3).

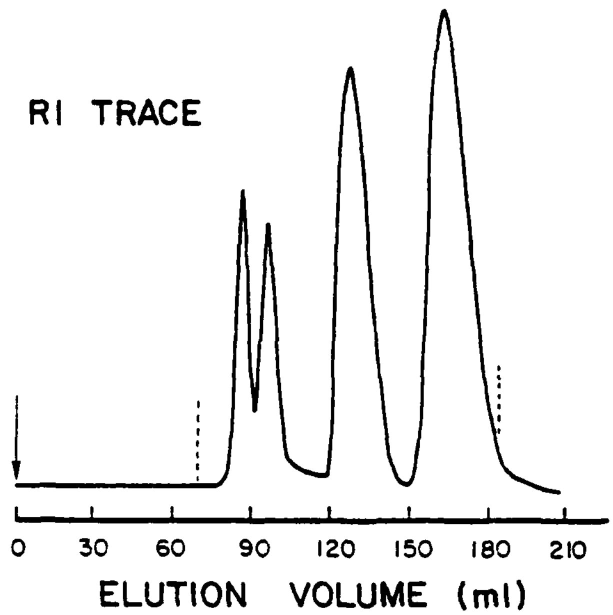
9. LC-^{1}HNMR profile for Jet Fuel JP-4 (spectral conditions same as indicated in Figure 3).

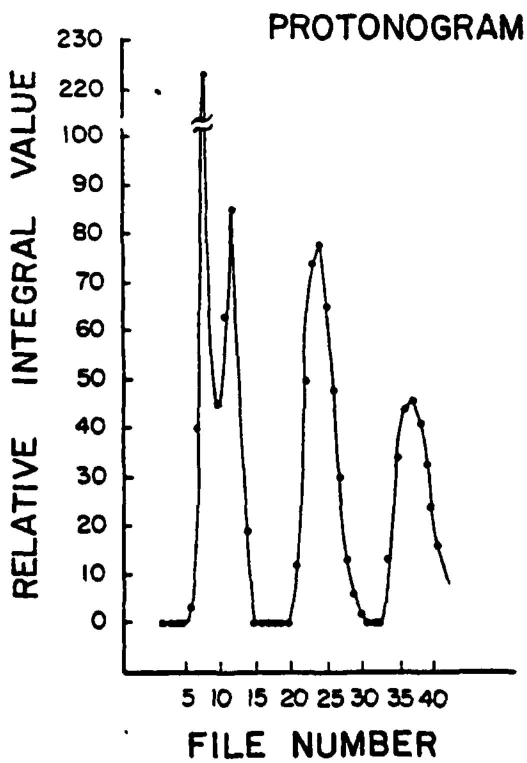
10. LC-^{1}HNMR profile for modified Jet Fuel JP-4 (spectral conditions same as indicated in Figure 3).

11. Refractive index trace for modified Jet Fuel JP-4.

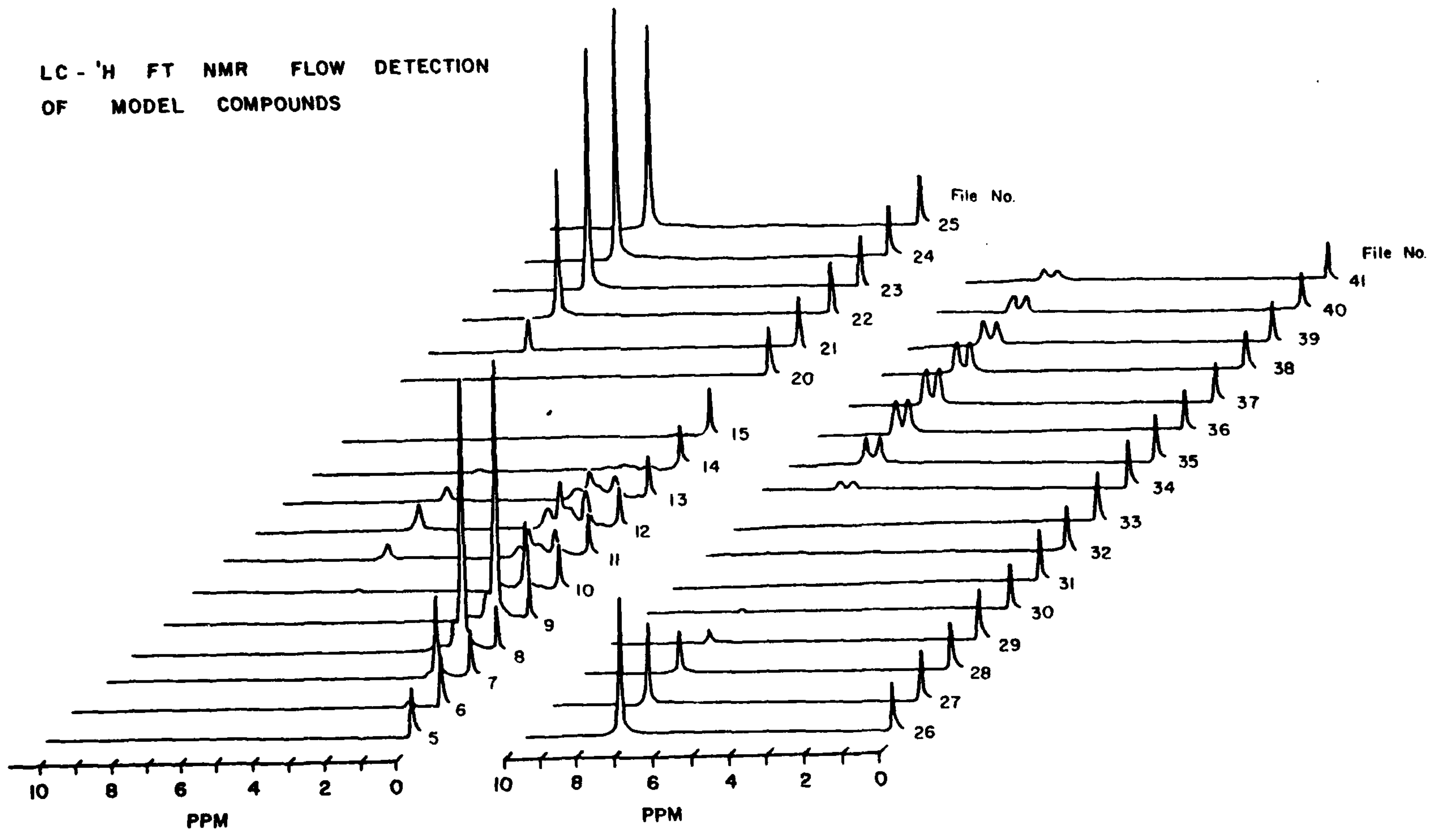
^{1}H FLOW NMR INSERT

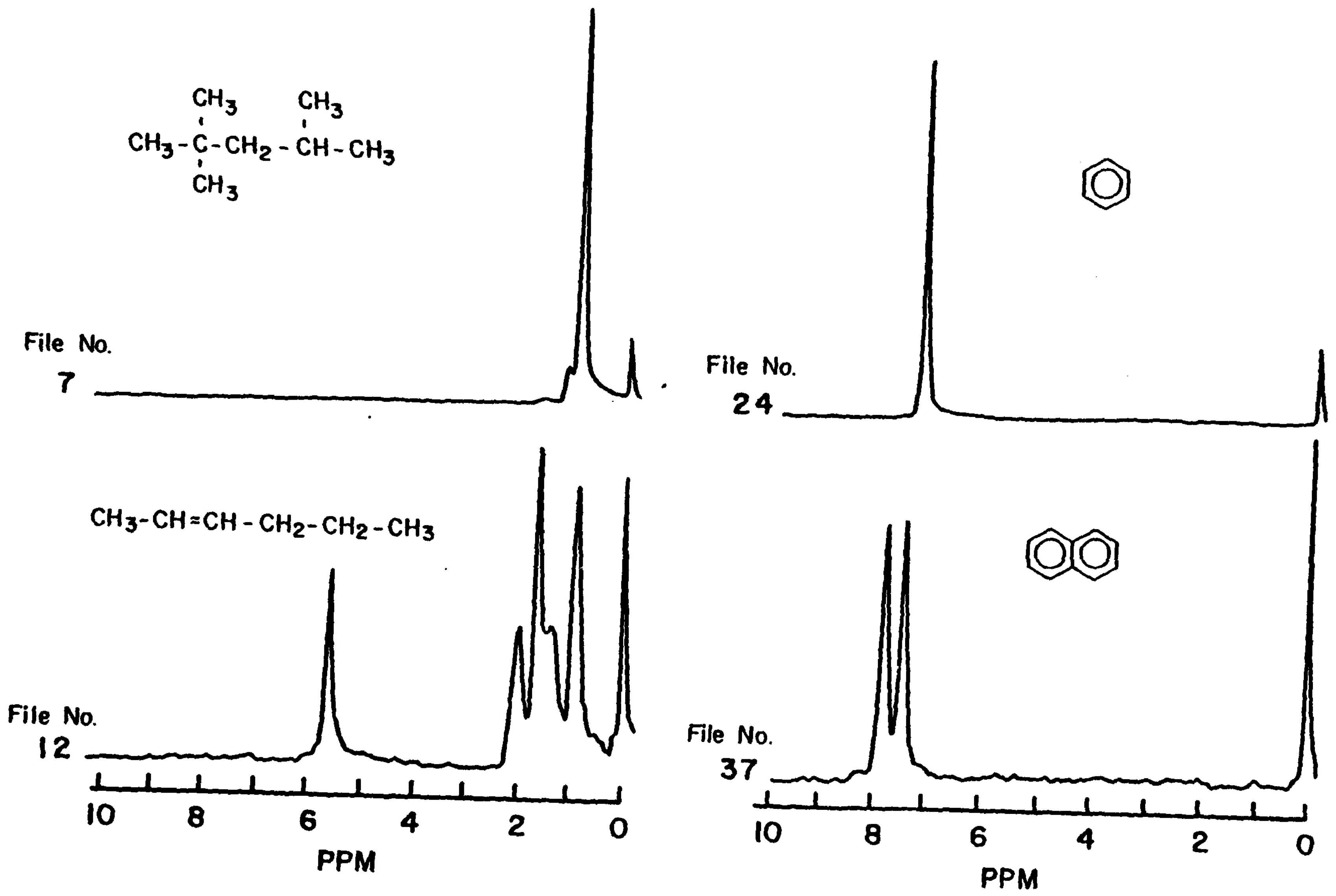



RI TRACE
0
30
60
90
120
150
180
210
ELUTION VOLUME (ml)


PROTONOGRAM
230
220
100
90
80
70
60
50
40
30
20
10
0
RELATIVE INTEGRAL VALUE
5
10
15
20
25
30
35
40
FILE NUMBER

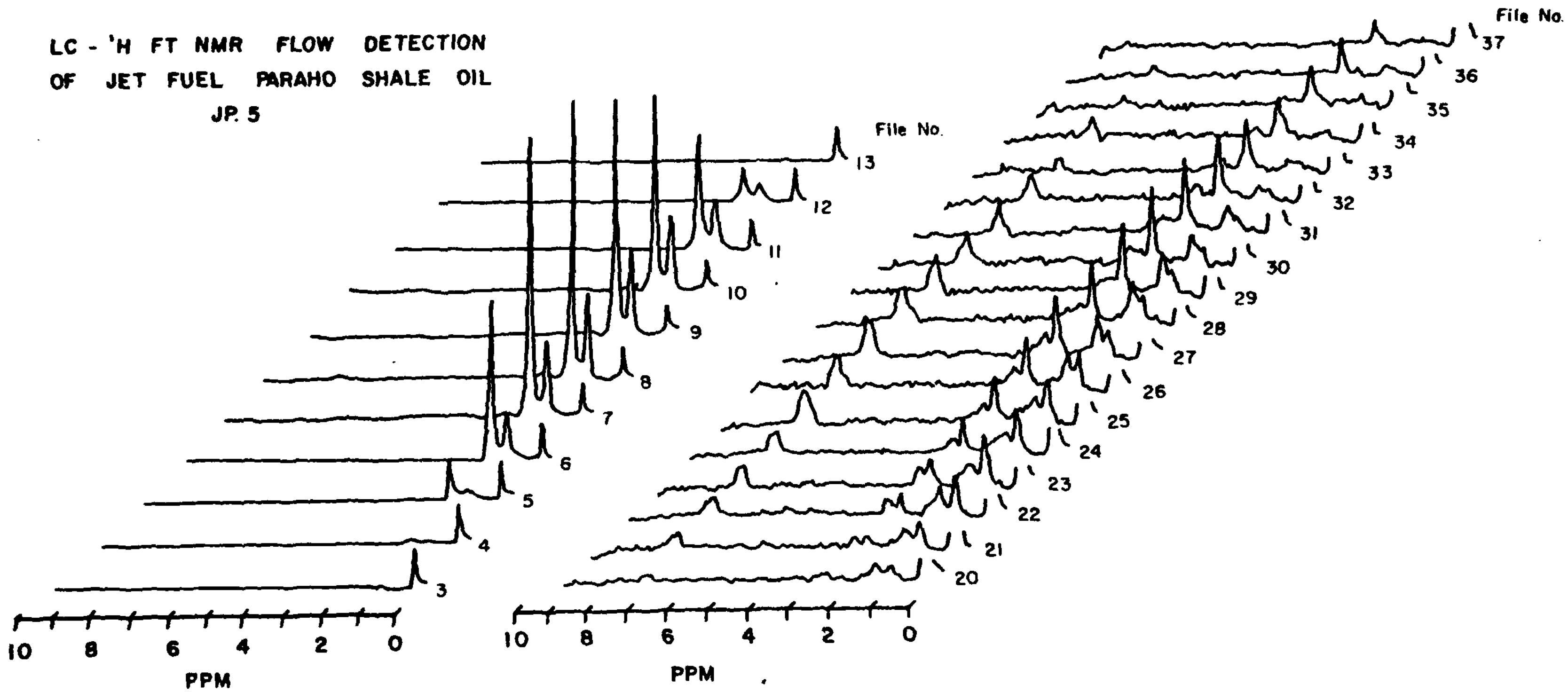
LC - ¹H FT NMR FLOW DETECTION OF MODEL COMPOUNDS

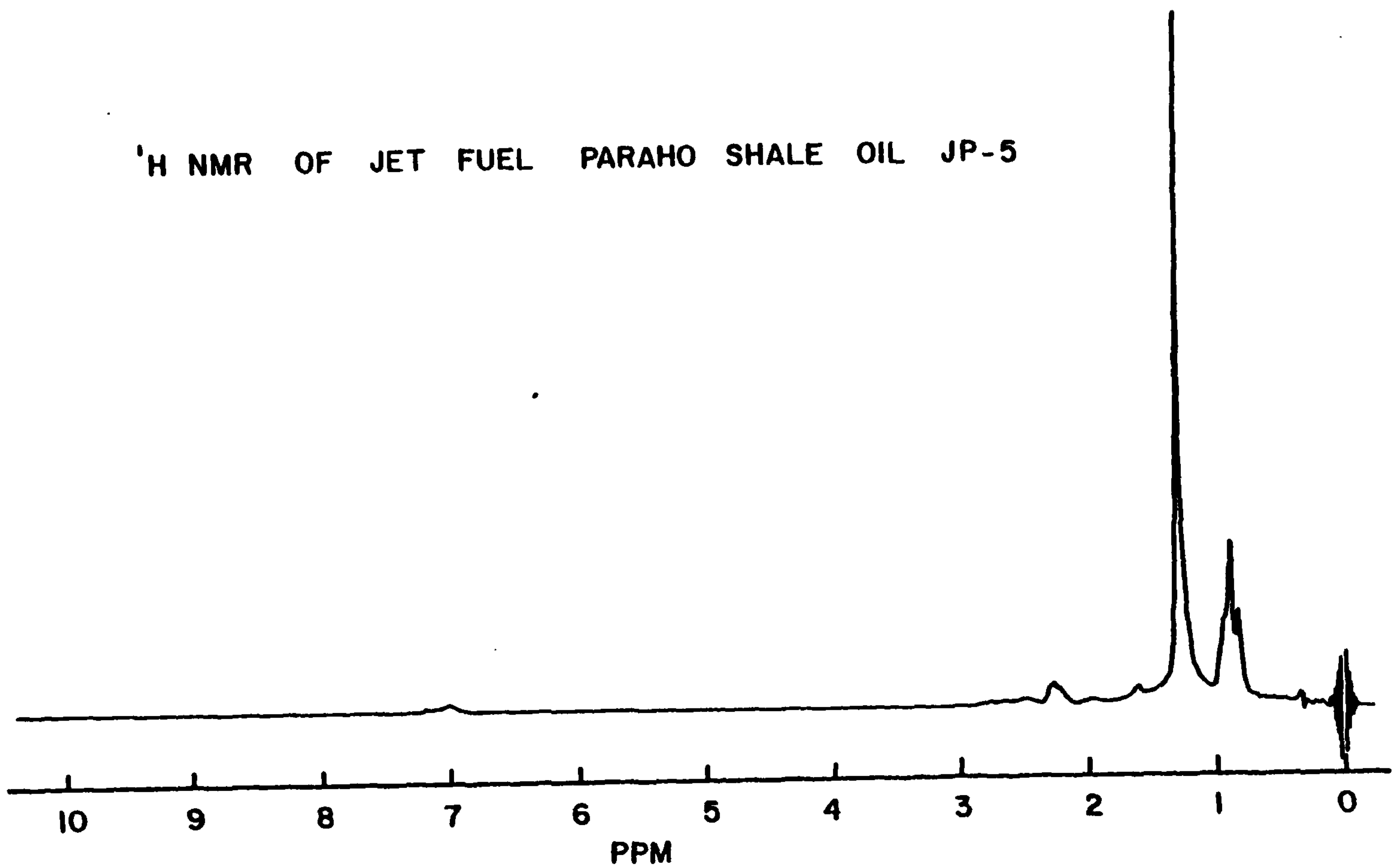




CH3 CH3
CH3-C-CH2-CH-CH3
CH3
File No.
7
File No.
24
CH3-CH=CH-CH2-CH2-CH3
File No.
12
10 8 6 4 2 0
PPM
File No.
37
10 8 6 4 2 0
PPM

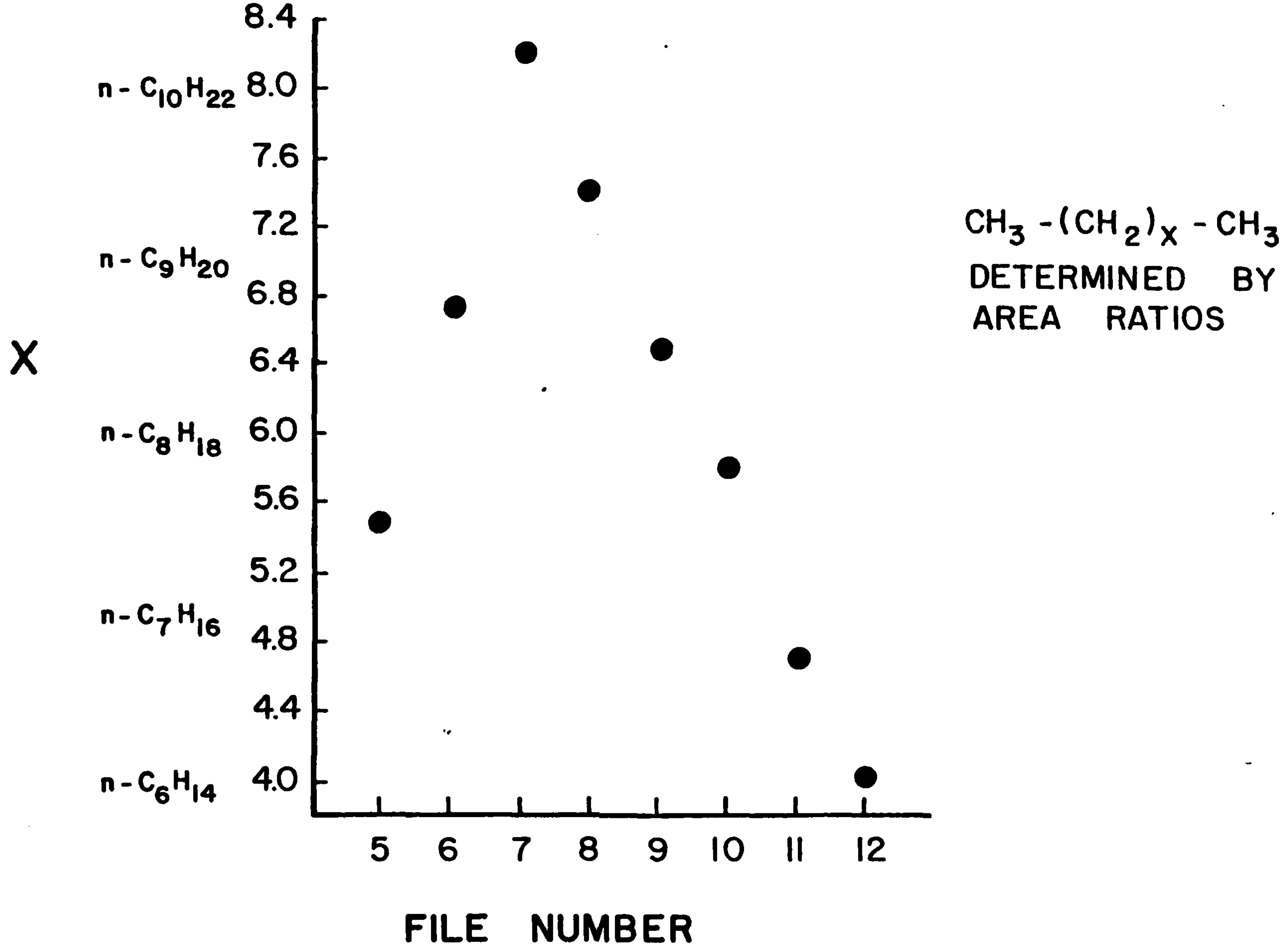
LC - ¹H FT NMR FLOW DETECTION
OF JET FUEL PARAHO SHALE OIL
JP. 5



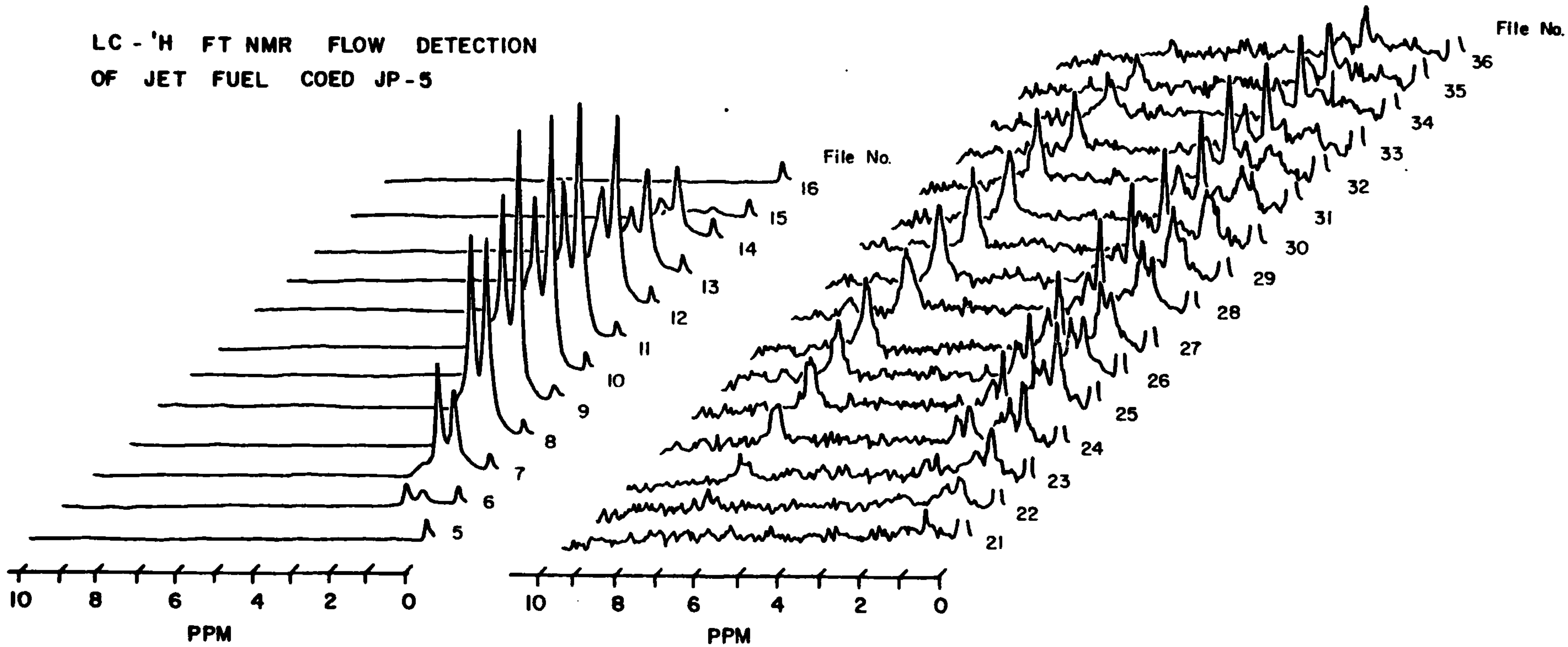


¹H NMR OF JET FUEL PARAHO SHALE OIL JP-5
10
9
8
7
6
5
4
3
2
1
0
PPM

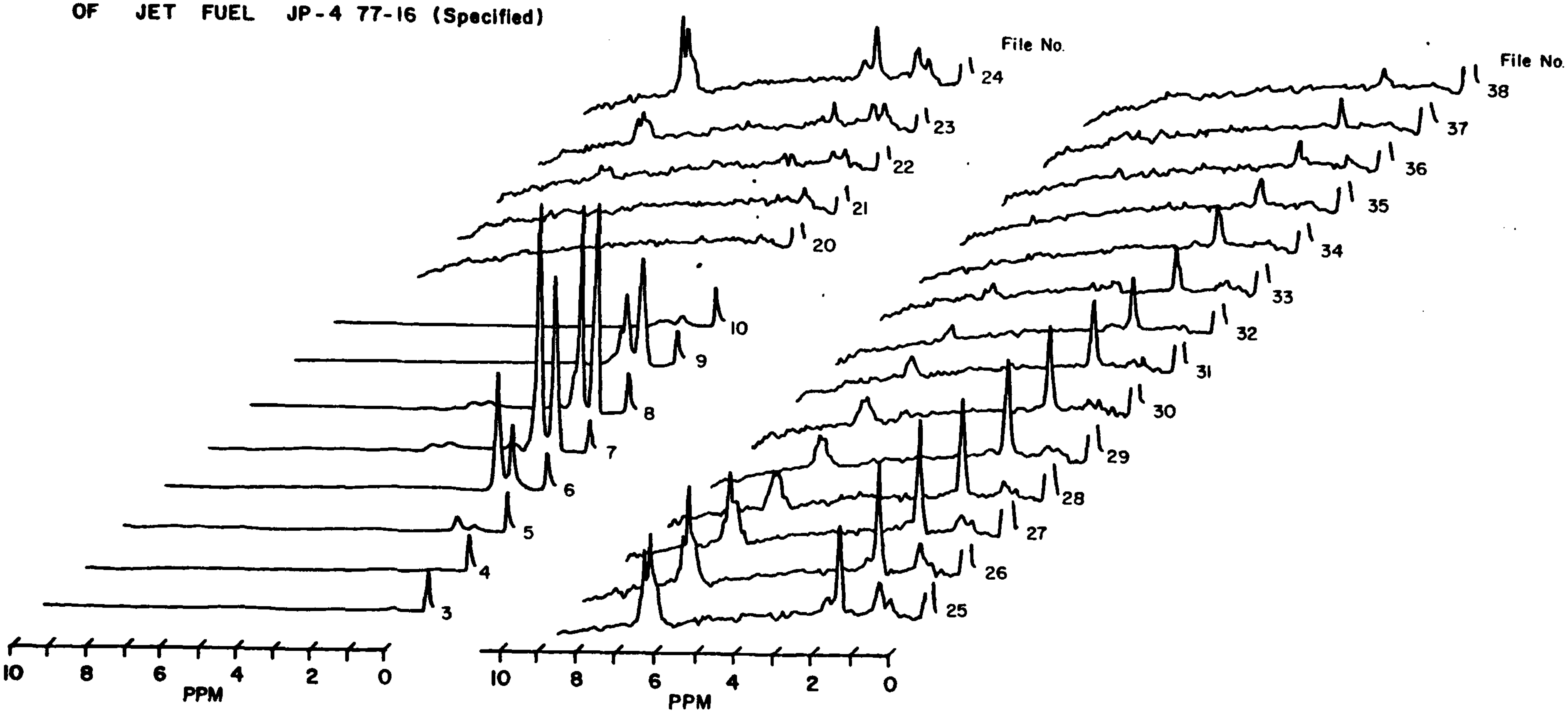
SHALE PARAHO ALIPHATIC PEAK



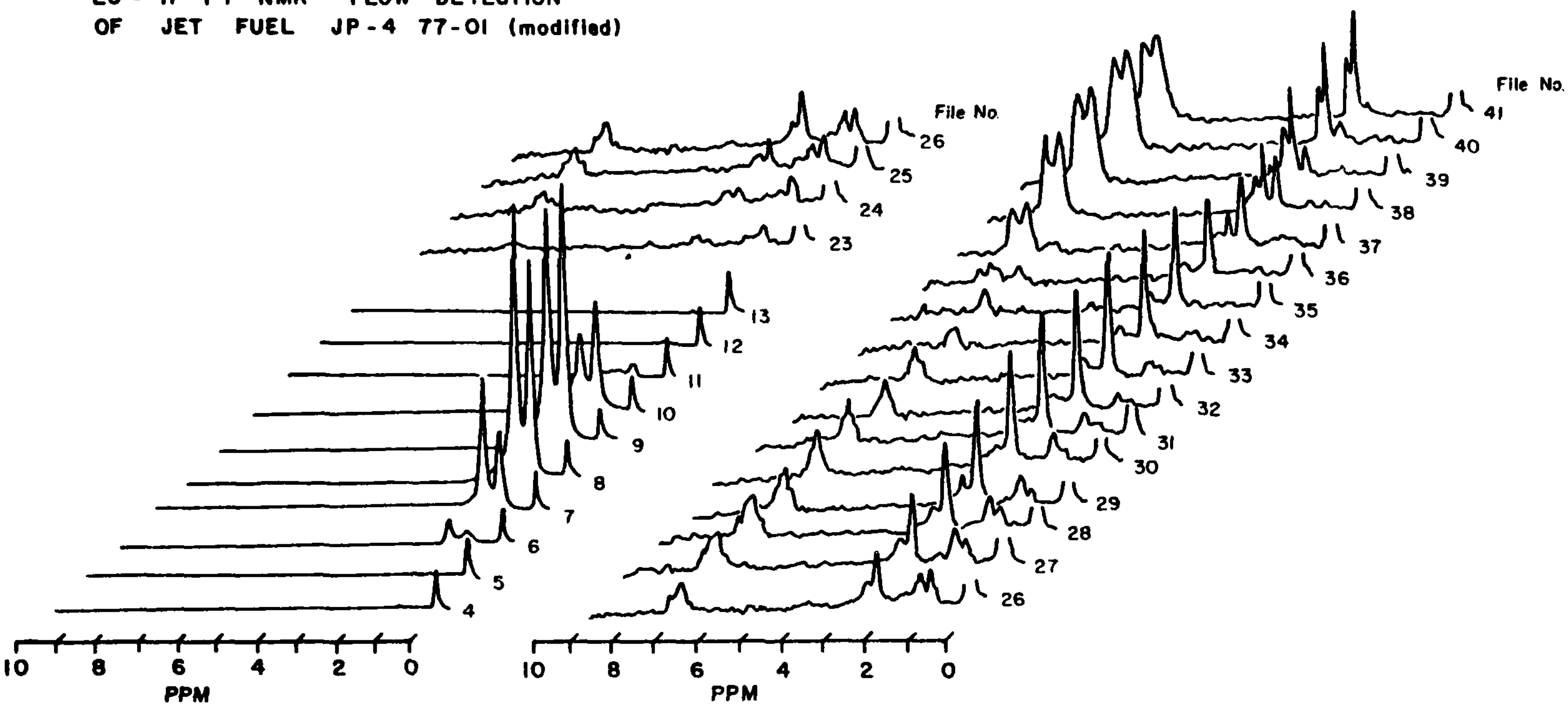
LC - [1]H FT NMR FLOW DETECTION
OF JET FUEL COED JP-5

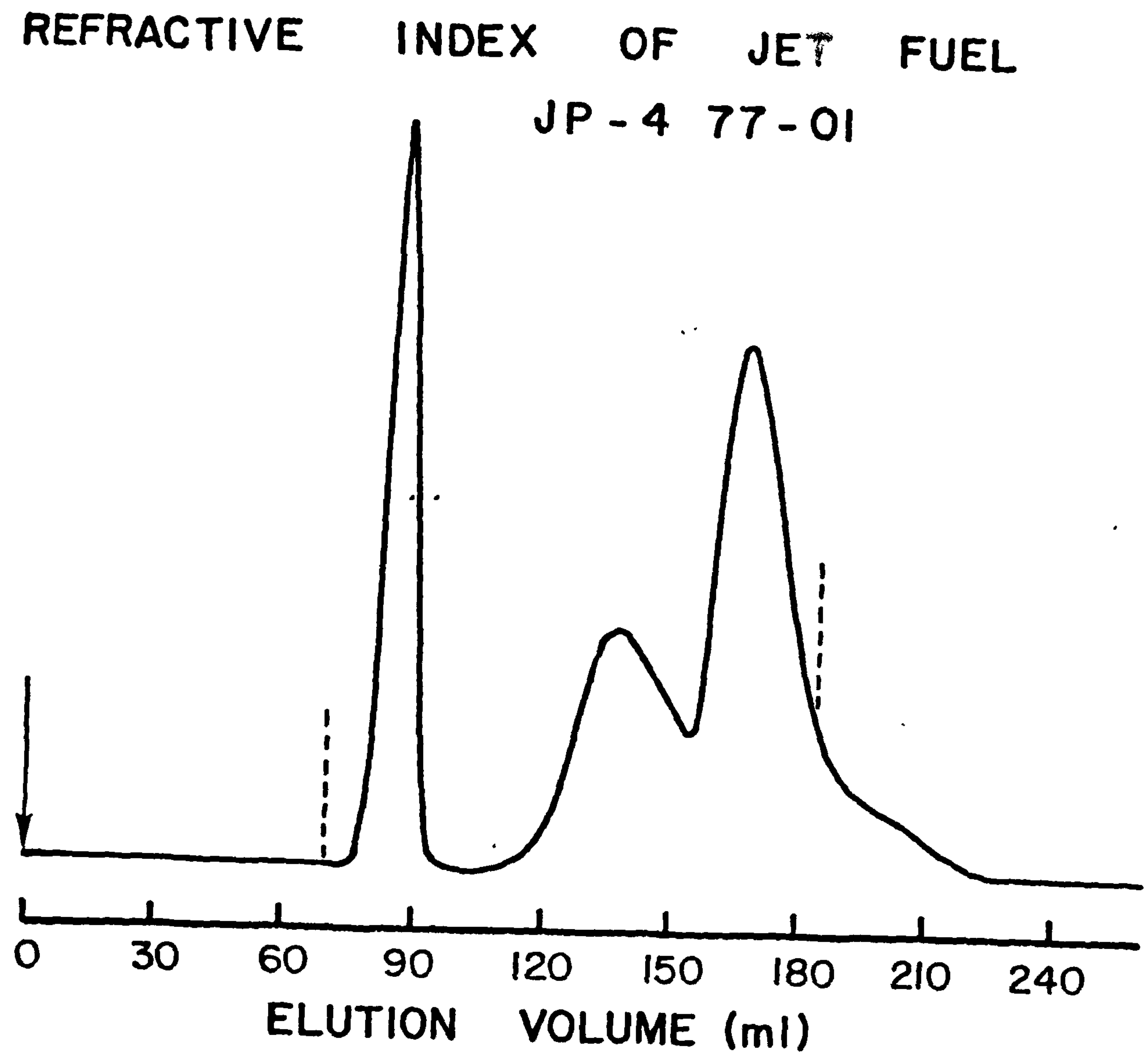


LC - ¹H FT NMR FLOW DETECTION
OF JET FUEL JP-4 77-16 (Specified)



LC - ^{1}H FT NMR FLOW DETECTION
OF JET FUEL JP-4 77-01 (modified)




REFRACTIVE INDEX OF JET FUEL
JP-4 77-01
0
30
60
90
120
150
180
210
240
ELUTION VOLUME (ml)